Large area quasi-free standing monolayer graphene on 3C-SiC(111)

U. Starke¹,a,* , C. Coletti¹,4,b, K.V. Emtsev¹,c, A.A. Zakharov²,d, T. Ouisse³,e and D. Chaussende³,f

¹Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany
²MAX-lab, Lund University, Lund, S-22100, Sweden
³Laboratoire des Matériaux et du Génie Physique - CNRS UMR5628 – Grenoble INP, Minatec 3 parvis Louis Néel, BP 257, 38016 Grenoble, France
⁴present address: Center for Nanotechnology Innovation @NEST, Istituto Italiano di Tecnologia, Piazza San Silvestro 12, 56127 Pisa, Italy

¹u.starke@fkf.mpg.de, ⑩camilla.coletti@iit.it, ⑫k.emtsev@fkf.mpg.de, ⑩alexei.zakharov@maxlab.lu.se, ⑩thierry.ouisse@grenoble-inp.fr, ⑩didier.chaussende@grenoble-inp.fr, *corresponding author

Keywords: Graphene, Intercalation, Quasi-free standing graphene, 3C-SiC, ARPES, AFM, LEEM, LEED, XPS

Abstract. Large scale, homogeneous quasi-free standing monolayer graphene is obtained on a (111) oriented cubic SiC bulk crystal. The free standing monolayer was prepared on the 3C-SiC(111) surface by hydrogen intercalation of a (6√3 × 6√3)R30°-reconstructed carbon monolayer, so-called zero-layer graphene, which had been grown in Ar atmosphere. The regular morphology of the surface, the complete chemical and structural decoupling of the graphene layer from the SiC substrate as well as the development of sharp monolayer π-bands are demonstrated. On the resulting sample, homogeneous graphene monolayer domains extend over areas of hundreds of square-micrometers.

Introduction

The growth of large scale, homogeneous graphene monolayers on the 4H and 6H polytypes of SiC by thermal decomposition of the topmost SiC layers has been investigated intensively [1,2]. In contrast, on cubic SiC substrates, namely the corresponding Si-face, i.e. 3C-SiC(111), just a few studies of graphene growth have been performed, yielding grain sizes of only a few micrometers and with limited homogeneity of the layers obtained [3-5]. The graphene layers presented so far on 3C-SiC(111) were grown on top of the carbon interface layer which couples by covalent bonds to the SiC substrate and by this coupling strongly influences the electronic structure of the graphene via doping [2]. In this paper, we present the preparation of homogenous, quasi-free standing monolayer graphene (QFMLG) on 3C-SiC(111) by growth in Ar atmosphere and subsequent hydrogen intercalation which yields domains extending over areas of hundreds of micrometers [6]. The morphological, structural and electronic properties are characterized.

Experimental Setup

The 3C-SiC(111) sample was cut from cubic SiC bulk material that had been grown on a 4H-SiC(0001) substrate by heteroepitaxy using the continuous feed-physical vapour transport (CF-PVT) method [7]. The 4H-SiC substrate was polished away after the growth process. Areas that were free of double positioning boundaries in the cubic crystal structure were selected and a sample of approximately 7 mm side length was obtained as shown in the photograph in Figure 1(a). Atomic force microscopy (AFM) was carried out in ambient environment. Graphene growth and hydrogen treatment were performed in a quartz glass reactor by induction heating (RF) of a graphite susceptor. The samples were characterized in ultra-high vacuum (UHV). The surface structure was analyzed by low-energy electron diffraction (LEED). The electronic structure was investigated by...
X-ray photoelectron spectroscopy (XPS) with Mg Kα radiation ($h\nu=1253.6$ eV) and angle-resolved photoemission spectroscopy (ARPES) using the He II line ($h\nu=40.8$ eV) from a UV discharge source. Low-energy electron microscopy (LEEM) was performed using the LEEM III instrument from ELMITEC.

**Homogeneous (6\sqrt{3} \times 6\sqrt{3})R30° Reconstruction on 3C-SiC(111)**

The high structural quality on an atomic level of the as grown 3C-SiC(111) sample surface is demonstrated in Figure 1(b) by AFM. The micrograph shown reveals atomically flat terraces with step heights around 1 nm as drawn from the line profile plotted in the inset. The (6\sqrt{3} \times 6\sqrt{3})R30° reconstructed initial carbon layer was grown on these substrates by RF heating in an Ar atmosphere (800 °C, 10 min, 800 mBar) [8]. This layer represents the buffer layer or zerolayer graphene (ZLG) which evolves prior to normal epitaxial graphene growth on SiC(0001). While growth in UHV leads to an inhomogeneous surface with small islands of different graphene thickness [9] as displayed in Figure 2(a), the RF method [8] – similar to the case of 4H and 6H-substrates – yields flat homogeneous layers with terrace widths in the 2-4 µm regime and step heights of about 8 nm, cf. Figure 2(b). The LEED pattern of the RF grown ZLG shows the fractional order spots of the (6\sqrt{3} \times 6\sqrt{3})R30° reconstruction around the first order diffraction spots of the SiC(111) substrate. At an electron energy of 188 eV as displayed in Figure 2(c), the extinction of three of these six first order spots corroborates the complete absence of twinning domains in the SiC substrate [6]. XPS of the C 1s core level shows – besides emission from the SiC substrate – two interface components as revealed from a line shape analysis, see panel (d). The two components, S1 and S2, correspond to the carbon species in the ZLG covalently bound to SiC, and the sp² hybridized carbon bound planar within the ZLG layer, respectively [2,10].

**Figure 1:** (a) Photograph of the 3C-SiC(111) sample (approx. 7mm on the long side) cut from the CF-PVT grown boule. (b) AFM micrograph for the as-grown 3C-SiC(111) sample. Inset: Height profile along the green line indicated in the main image.

**Figure 2:** AFM micrographs of (a) a UHV grown ZLG and (b) an RF-grown ZLG on 3C-SiC(111). The insets display height profiles along the green lines indicated in the respective images (hor. axis: µm, vert. axis: nm). (c) LEED pattern of an RF-grown ZLG at 188 eV. (d) C1s core level spectrum for RF-grown ZLG. Spectral components obtained from a line shape analysis are indicated. S1 and S2 reflect carbon within the ZLG, S1 covalently bound to SiC, and S2 sp² hybridized and planar within the ZLG, SiC indicates emission from carbon in the bulk crystal.
Growth of QFMLG on 3C-SiC(111)

Subsequently, the sample was processed by annealing to around 850 °C in a molecular hydrogen flow at atmospheric pressure. While due to the covalent bonds between as grown ZLG and the SiC substrate the px-orbitals of the carbon atoms cannot form a delocalized π-system [2], after the hydrogen treatment sharp π-bands evolve as measured by ARPES and plotted in Figure 3(a). This indicates that the ZLG was turned into QFMLG by hydrogen intercalation [11]. In this state, the dangling bonds of the topmost Si atoms of the substrate are passivated by hydrogen and the carbon layer is decoupled from the SiC substrate as corroborated by the suppression of the reconstruction spots in LEED, cf. Figure 3(b), and by the disappearance of the interface components S1 and S2 in XPS, whereas a sharp emission line emerges from the graphene layer (indicated by “g”), as seen in Figure 3(c). However, in contrast to quasi-free standing graphene on hexagonal SiC crystals [11], the π-band dispersion of the QFMLG on 3C-SiC(111) indicates a notable n-type doping, see panel (a), which requires further investigation. LEEM images acquired on a large field of view (~57 µm) demonstrate an extremely homogeneous graphene thickness over the entire surface, as indicated by the lack of contrast in the grayscale as shown in panel (d). At a larger magnification (~23 µm), details of the surface morphology can be observed, cf. panel (e). A darker contrast, symptomatic of a different graphene thickness, emerges only at the step edges (see panel e) or in restricted domains, see panel (d). Electron reflectivity spectra extracted from energy series of such LEEM images can be used to count the number of graphene layers present [12] by counting the number of minima in the energy range between 0 and 6 eV. Such spectra evaluated for areas of different contrast in the region shown in panel (e) and plotted in panel (f) confirm that practically the entire surface is covered by monolayer graphene (areas with grey contrast in panel e, analyzed regions are labeled A

Figure 3: QFMLG on 3C-SiC(111) after hydrogen intercalation of RF-grown ZLG: (a) ARPES measurement of the π-band dispersion at the K-point of the graphene Brillouin zone, acquired perpendicular to the KΓ-direction. (b) Micro-LEED image taken at 98 eV. Arrows indicate first order diffraction spots for graphene (solid lines) and SiC (dashed lines). (c) C1s core level spectrum with fitted components indicated for graphene (g) and SiC bulk emission, respectively. (d) LEEM overview image (energy E=19 eV, ~57µm field of view (FOV)). (e) LEEM micrograph (E=4 eV, ~23µm FOV). Representative regions are labeled with A, B and C. (f) Electron reflectivity spectra measured for regions A, B and C in panel (e). Curve C is shifted on the y-axis for better display.
and B) while bilayer graphene is only present at the darker step edges (region C). We note that, in contrast to as grown graphene on SiC(0001) [12], an extra minimum appears above 6 eV, whose origin is not yet clear at present. We observe areas of lighter gray contrast that are running along certain crystal orientations (region B). Nevertheless, they are clearly identified as monolayer graphene also by the LEEM intensities. Hence, the contrast difference is not due to the graphene properties. We speculate that it could be caused by defects in the substrate, which might be mediated by strain. LEEM analysis also reveals that the large atomically flat macro-terraces that are homogeneously covered by QFMLG run uninterrupted for hundreds of micrometers. This thickness homogeneity is highly remarkable considering that, until now, the maximum lateral dimension reported for homogenous graphene domains on SiC(111) was roughly 1 µm [3-5].

Summary

In conclusion, this work demonstrates that large area QFMLG can be produced on 3C-SiC(111) substrates. The high quality of the graphene layer obtained suggests that 3C-SiC(111) might be an appealing and cost effective platform for the future development of graphene technology.

Acknowledgements

C.C. acknowledges the Alexander von Humboldt Foundation for financial support. This research was partially funded by the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 226716. We are indebted to the staff at MAX-Lab (Lund, Sweden) for their advice and support.

References

[1] U. Starke and C. Riedl, J. Phys.: Cond. Mat. 21 (2009) 134016.
[2] C. Riedl, C. Coletti and U. Starke, J. Phys. D: Appl. Phys. 43 (2010) 374009.
[3] A. Ouerghi, R. Belkhou, M. Marangolo, M.G. Silly, S. El Moussaoui, M. Eddrief, L. Largeau, M. Portail and F. Sirotii, Appl. Phys. Lett. 97 (2010) 161905.
[4] A. Ouerghi, A. Kahouli, D. Lucot, M. Portail, L. Travers, J. Gierak, J. Penuelas, P. Jegou, A. Shukla, T. Chassagne and M. Zielinski, Appl. Phys. Lett. 96 (2010) 191910.
[5] A. Ouerghi, M. Marangolo, R. Belkhou, S. El Moussaoui, M. G. Silly, M. Eddrief, L. Largeau, M. Portail, B. Fain and, F. Sirotii, Phys. Rev. B 82 (2010) 125445.
[6] C. Coletti, K.V. Emtsev, A.A. Zakharov, T. Ouisse, D. Chaussende and U. Starke, Appl. Phys. Lett. 99 (2011) 081904.
[7] D. Chaussende, L. Latu-Romain, L. Auvrav, M. Ucar, M. Pons and R. Madar, Mat. Sci. Forum 483-485 (2005) 225.
[8] K.V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G.L. Kellogg, L. Ley, J.L. McChesney, T. Ohta, S.A. Reshanov, E. Rotenberg, A.K. Schmid, D. Waldmann, H.B. Weber and T. Seyller, Nat. Mater. 8 (2009) 203.
[9] C. Riedl, U. Starke, J. Bernhardt, M. Franke and K. Heinz, Phys. Rev. B 76 (2007) 245406.
[10] K.V. Emtsev, F. Speck, Th. Seyller, L. Ley and J.D. Riley, Phys. Rev. B 77 (2008) 155303.
[11] C. Riedl, C. Coletti, T. Iwasaki, A.A. Zakharov and U. Starke, Phys. Rev. Lett. 103 (2009) 246804.
[12] H. Hibino, H. Kageshima, F. Maeda, M. Nagase, Y. Kobayashi and H. Yamaguchi, Phys. Rev. B 77 (2008) 075413.