Quasi-free-standing monolayer and bilayer graphene growth on homoepitaxial on-axis 4H-SiC(0001) layers

Jawad ul-Hassan, M. Winters, Ivan Gueorguiev Ivanov, O. Habibpour, H. Zirath, N. Rorsman
and Erik Janzén

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Jawad ul-Hassan, M. Winters, Ivan Gueorguiev Ivanov, O. Habibpour, H. Zirath, N. Rorsman and Erik Janzén, Quasi-free-standing monolayer and bilayer graphene growth on homoepitaxial on-axis 4H-SiC(0001) layers, 2015, Carbon, (82), 12-23.

<http://dx.doi.org/10.1016/j.carbon.2014.10.010>

Copyright: Elsevier

<http://www.elsevier.com/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-113151>

Quasi-free-standing monolayer and bilayer graphene growth on homoepitaxial on-axis 4H-SiC(0001) layers

J. Hassan^{*1}, M. Winters², I. G. Ivanov¹, O. Habibpour², H. Zirath², N. Rorsman² and E. Janzén¹

¹Department of Physics, Chemistry and Biology, Linköping University,
SE-581 83 Linköping, Sweden

²Department of Microtechnology and Nanoscience, Chalmers University of Technology,
Kemivägen 41296 Göteborg, Sweden

Abstract

Quasi-free-standing monolayer and bilayer graphene is grown on homoepitaxial layers of 4H-SiC. The SiC epilayers themselves are grown on the Si-face of nominally on-axis semi-insulating substrates using a conventional SiC hot-wall chemical vapor deposition reactor. The epilayers were confirmed to consist entirely of the 4H polytype by low temperature photoluminescence. The doping of the SiC epilayers may be modified allowing for graphene to be grown on a conducting substrate. Graphene growth was performed via thermal decomposition of the surface of the SiC epilayers under Si background pressure in order to achieve control on thickness uniformity over large area. Monolayer and bilayer samples were prepared through the conversion of a carbon buffer layer and monolayer graphene respectively using hydrogen intercalation process. Micro-Raman and reflectance mappings confirmed predominantly quasi-free-standing monolayer and bilayer graphene on samples grown under optimized growth conditions. Measurements of the Hall properties of Van der Pauw structures fabricated on these layers show high charge carrier mobility ($>2000 \text{ cm}^2/\text{Vs}$) and low carrier density ($<0.9 \times 10^{13} \text{ cm}^{-2}$) in quasi-free-standing bilayer samples relative to monolayer samples. Also, bilayers on homoepitaxial layers are found to be superior in quality compared to bilayers grown directly on SI substrates.

*Corresponding author. Email: jawul@ifm.liu.se (Jawad Ul Hassan)

1. Introduction

Epitaxial growth of graphene on semi-insulating (SI) SiC has the potential to enable next generation ultra high frequency and low power electronic devices [1-6]. The main advantage is the possibility to obtain large area graphene directly on SI substrates which is one of the main requirements for high frequency devices. A lot of efforts have been made during the last decade on the growth of graphene on SiC using different techniques and growth mechanisms [7-11]. The growth process is mainly based on the thermal decomposition of the substrate surface at high temperature under ultra high vacuum or under argon background pressure. Silicon sublimates from the surface layers while the carbon atoms left behind on the surface form a carbon buffer layer and graphene layer(s). Epitaxial growth of a few layer graphene on SiC has also shown to be possible through chemical vapor deposition of carbon on the surface using propane as a source gas under optimized growth conditions [12, 13]. Other methods to obtain large area graphene include chemical vapor deposition (CVD) growth on metals [14-16]. However, the CVD on metal process is less suitable for device fabrication as the graphene layers must be transferred onto a semiconducting or SI substrate [17]. These transferred graphene layers tend to be both defected and contaminated as a result of the transfer process, thus resulting in graphene which is not suitable for device oriented applications [18].

High frequency electronic devices require electrical isolation which is achieved through the growth of active layer structure on SI substrates. The Si-face of nominally on-axis 4H-SiC substrates is preferred over the C-face for the growth of graphene. This is mainly due to the fact that graphene growth is easier to control on the Si-face and under optimized growth conditions the thickness of the graphene can be limited to just a few layers over large areas. On-axis substrates are used in order to avoid a high surface step density thereby facilitating the growth of very uniform graphene monolayers and bilayers over large areas of the substrate.

Monolayer and bilayer graphene are of particular importance due to their unique physical properties. Monolayer and bilayer graphene exhibits a high carrier mobility which is suitable for high frequency electronics. Pristine monolayer graphene is a semi-metal with zero bandgap and does not allow high on/off ratio (a basic requirement for switching devices). On the other hand, bilayer graphene has shown to open up a narrow bandgap of 100-250 meV in the presence of potential gradient across the two adjacent layers [19-23]. The potential can be created either

through different doping levels in the adjacent layers or by applying external electrical potential across the structure. The latter method is more practical and also allows tuning of the bandgap during device operation. An external potential can be applied through dual gating of the device via top- and back-gating. This idea has so far been only tested on exfoliated graphene flakes on SiO₂ which are not suitable for large scale production.

In order to be able to apply potential gradient across adjacent layers of graphene on SI substrates, a conductive layer with controlled doping is needed underneath the graphene layers. Such a conductive layer can be obtained through homoepitaxial growth on the Si-face of nominally on-axis 4H-SiC substrate using CVD; a wide range of conductivity can be obtained in the epitaxial SiC through controlled doping. In this work we report the details of our approach of the growth of graphene on homoepitaxial layers of 4H-SiC – grown on nominally on-axis SI substrates – as well as the structural and electronic properties obtained. The structure can be used for back-gated electronic devices such as graphene-based high-frequency field-effect transistors (GFETs).

2. Material Growth

Homoepitaxial layers were grown with controlled n-type doping on the Si-face of nominally on-axis (unintentional off-cut < 0.05°) SI 4H-SiC substrates. Graphene was then grown and in-situ intercalated with hydrogen.

The Si face of the substrates are chemo-mechanically polished providing a smooth surface prior to epitaxial growth. Large 16x16mm² pieces diced from a single wafer were used in this study. All of the growth processes and substrate surface preparations were performed in a conventional horizontal hot-wall CVD reactor, mainly used for the growth of SiC layers. The heating zone of the reactor is equipped with SiC-coated high purity graphite susceptor while the heating is implemented using RF-induction. The temperature is measured using a pyrometer facing to the ceiling of the susceptor directly above the substrate and can be controlled up to 1900 K. The reactor is also equipped with high-throughput turbomolecular pump which can maintain high vacuum level down to 1x10⁻⁵ Pa.

2.1 Homoepitaxial growth of 4H-SiC

Epitaxial growth on the Si-face of nominally on-axis 4H-SiC substrates under standard growth conditions leads to the formation of 3C-inclusions and other defects in the epilayer. In this study we have used our unique growth process developed for on-axis homoepitaxy, which allows us to obtain pure 4H polytype in the epilayer without inclusions of foreign polytypes [24].

In the case of standard homoepitaxial growth on off-cut substrates (4° off-cut), in-situ surface preparation of substrate is performed in a background pressure of hydrogen at high temperature in order to remove subsurface damages. The epitaxial growth is then performed at the C/Si ratio of 1. In the case of on-axis epitaxy, we have observed that in-situ surface preparation of the substrate and growth in slightly Si-rich environment together with slightly higher growth temperature plays a key role in the replication of the substrate polytype into the epilayer. Surface preparation under such conditions reveals more uniform surface step structure mainly composed of large steps that are usually about 10-40 nm and small steps that are 0.5-1 nm [25]. The small steps originate from threading screw dislocations intersecting the surface while the large steps are related to small unintentional off-cut in the substrate and surface step-bunching on the Si-face. In-situ etching conditions were optimized to minimize the formation of large steps and preferential etching around dislocations. Homoepitaxial growth was performed at a growth temperature of about 1870 K and a pressure of 1×10^3 Pa. The epitaxial layers were grown at growth rate of $7 \mu\text{m/h}$ to a total thickness of 2-3 μm using silane and propane as silicon and carbon sources. Since surface roughness is known to increase drastically with thickness, thin layers were grown in order to avoid large surface inhomogeneities [26]. The layers were grown with a controlled n-type doping of $1 \times 10^{16} \text{ cm}^{-3}$ using nitrogen gas as dopant. The doping level in the reference epilayers was confirmed via capacitance-voltage (CV) measurements using a mercury probe.

The surface morphology of on-axis homoepitaxial layers observed using optical microscope with Nomarski contrast, displays a relatively inhomogeneous surface. These inhomogeneities are due to different growth mechanisms active in different regions of the epilayer and to heavy surface step-bunching native to the Si-face of SiC (Fig. 1). In the case of off-cut substrates (e.g., 4° or 8° off-cut) the epitaxial growth is driven by step-flow growth which results in very smooth surface whereas in the case of on-axis substrates the growth can be a mixture of step-flow (Fig. 1a) and spiral growth (Fig. 1b) which together with step-bunching leads to rougher surface. However, very large areas completely free of large steps are also observed, as illustrated in Fig. 1c.

Fig. 1 Optical images taken from different regions of as-grown on-axis epilayer revealing different surface morphologies (a) large steps on the surface (b) spiral growth and (c) relatively large smooth region. AFM images in (d), (e) and (f) show the corresponding surface step structure over $100 \times 100 \mu\text{m}^2$ areas while high magnification images taken from the marked regions show detailed surface step structure. Horizontal lines in image (d) are measurement artifact.

The surface of the homoepitaxial layers was also characterized with tapping mode atomic force microscopy (AFM). Regions which are dominated with step flow growth (Fig. 1a) demonstrate large steps with heights on the order of 20-200 nm separated by $>100 \mu\text{m}$ wide regions which are relatively smooth (Fig 1d). These relatively smooth regions are covered with a fine step structure of 0.5-1 nm steps while the edges of large steps are covered with larger 1-4 nm steps (Fig. 1d). Spiral growth regions (Fig. 1b) appears to be relatively flat with arm-like features pointing towards $[1\bar{1}20]$ directions (Fig. 1e). The regions which appear very smooth under the optical

microscope (Fig 1c) are also found to be dominated by the spiral growth mode interlaced with fine 0.5-1.0 nm steps (Fig. 1f).

The epilayers were confirmed to be 100% of the 4H polytype by measuring the low temperature photoluminescence (PL) spectrum on random areas. The spectra did not show any PL emission related to foreign polytype inclusions. The near band gap emission spectrum is dominant with sharp nitrogen-bound exciton lines. The free-exciton lines are also visible at this doping level reflecting the high purity and quality of epilayers.

2.2 Growth of monolayer and bilayer graphene under Si ambient

After homoepitaxial growth, the samples were loaded in the reactor along with reference pieces (bare substrate pieces from the same wafer used for the homoepitaxial growth) and surface preparation was made in hydrogen in the temperature range of 1670-1770 K and pressure of 1×10^3 Pa for a few minutes to remove the native oxide. The reference samples were used to compare the surface morphology, graphene thickness and uniformity with those on homoepitaxial layers. We introduce a new approach of graphene growth under Si background pressure to have better control on the number of layers and thickness uniformity over large area whereas the growth process is still based on thermal decomposition of the surface through sublimation of Si. The growth was performed under Si background pressure of $(0.6 - 1) \times 10^{-3}$ Pa in the temperature range of 1670-1770 K for 60 minutes.

When graphene is grown under vacuum, the thickness and uniformity are controlled exclusively by the growth temperature [11, 27]. This is due to high preferential removal rate of Si at step edges [28, 29] and around threading screw dislocations intersecting the surface. This removal rate can be controlled to some extent via a combination of a relatively low growth temperature and a high background pressure of Si.

The excess Si over SiC substrate efficiently suppresses the decomposition rate of the surface by reducing the removal rate of Si from the surface. Additionally, high background pressure also allows for high temperature growth through shifting the surface phase transitions towards higher temperatures. Higher pressures lead to the formation of relatively high quality graphene with large domains. The process is compatible with the growth system and is easy to control. The Si background pressure during the growth of graphene was achieved through the evaporation of excess Si from the inner side of the susceptor that was deposited intentionally during a separate

Fig. 2 A schematic illustration of graphene growth process on homoepitaxial layers. For quasi-free-standing monolayer samples, only the carbon buffer layer was grown, whereas for quasi-free-standing bilayer samples, C-buffer layer plus monolayer graphene was grown. Hydrogen intercalation transformed the carbon buffer layer sample into quasi-free-standing monolayer and C-buffer layer plus monolayer sample into quasi-free-standing bilayer graphene. The step edges in both cases show one additional graphene layer.

preceding growth run. The deposition process of excess Si was also optimized in order to achieve constant silicon background pressure during the whole growth run of graphene. The Si ambient pressure as well as the growth temperature is found to be the main factors which control the thickness of graphene and its uniformity over large areas.

The growth processes were optimized to obtain quasi-free-standing monolayer and bilayer graphene under Si background pressure. In order to obtain quasi-free-standing monolayer graphene, only the carbon buffer layer was grown, whereas when bilayer graphene was desired, the growth conditions were optimized to obtain monolayer graphene on the surface of homoepitaxial 4H-SiC layers (Fig. 2). Subsequent hydrogen intercalation transformed the carbon buffer layer into quasi-free-standing monolayer, and the monolayer graphene into quasi-free standing bilayer graphene (Fig. 2). The whole growth process including substrate surface preparation, on-axis homoepitaxial growth, graphene growth and hydrogen intercalation can also

Fig. 3 Optical images (a) and (b) taken after the growth of bilayer graphene on 2-3 μm thick epilayer, and (c) taken from the reference sample, which is a bare substrate grown during the same growth run. (d) AFM image taken from region similar to (a) shows large 20 nm step on the surface; the high magnification image taken from the marked region reveals that the large step is built of 2-6 nm steps. (e) AFM image taken from the reference sample; the high magnification image taken from the marked region shows 2-6 nm steps on the surface.

be performed in a single sequence without exposing the samples to air. However, in this study, the samples were removed from the reactor after homoepitaxial growth in order to study the properties of the 4H-SiC layers. The subsequent graphene growth and hydrogen intercalation was performed in a single growth process without exposing the samples to air.

As mentioned in the previous section, the surface morphology of the homoepitaxial layer is mainly dominated by large steps and the regions between them are covered with small steps of 0.5-1 nm height. Graphene growth on such surfaces does not seem to alter the structure of the large steps (Fig. 3a) formed through either surface step-bunching or spiral-growth related arm-like features. However, the 0.5-1 nm steps covering the wide regions between large steps on as-grown epilayer surface coalesce to form 2-4 nm steps leaving relatively wide atomically flat terraces during graphene growth (Fig.3d). This is more clearly demonstrated in Fig. 4, where

Fig. 4 AFM images taken from (a) as-grown epilayer surface covered with 0.5-1 nm steps and (b) the same epilayer after graphene growth. The micro-step structure on as-grown epilayer surface in (a) coalesce to form relatively larger steps 2-4 nm and wider terraces 2-5 μm after graphene growth in (b).

Fig. 4(a) is AFM image taken after the growth of homoepitaxial layer whereas Fig. 4(b) is taken after the growth of graphene. By comparing these two images one observes that the 0.5-1 nm steps on the homoepitaxial layer transform into 2-4 nm steps and consequently the width of atomically flat terraces is also increased. Similar behavior of the rearrangement of surface step-structure was also observed in monolayer and bilayer graphene samples. Featureless and very smooth regions of the as-grown epitaxial layers also seem to degrade through the coalescence of 0.5-1 nm steps into 2-4 nm steps as a result of surface step-bunching during graphene growth. Furthermore, features related to step-bunching in smooth regions also appear under optical microscope (Fig. 3b) after graphene growth.

The reference sample on the other hand does not show any large steps on the surface although the surface is still step-bunched with step height of 2-4 nm (Fig. 3c and e). The absence of large steps is mainly due to substrate surface preparation at low temperature and pressure and the subsequent growth under background pressure of Si. Similar reconstruction of 0.5-1 nm steps into 2-4 nm steps has been reported during graphene growth in vacuum on bare substrates that were

etched in hydrogen prior to the growth of graphene [30]. However, in this case, large steps are also observed on the surface due to high temperature surface preparation.

Low temperature growth under controlled Si background pressure leads only to the formation of a carbon buffer layer on wide terraces and narrow strips of monolayer graphene (about 1 μm width) formed on step edges. Hydrogen intercalation transforms the buffer layer on wide terraces into quasi-free-standing monolayer while at the step-edges, narrow strips of quasi-free-standing bilayers are formed.

A relatively high growth temperature is used for the growth of the carbon buffer layers plus monolayer graphene under the same ambient conditions. This leads to the formation of monolayer graphene on wide terraces decorated with narrow stripes of bilayer graphene only along the step edges. Hydrogen intercalation transforms monolayer graphene on the wide terraces into bilayer graphene whereas bilayer graphene along the step edges is transformed into a trilayer. The stripes of trilayer along the step edges in bilayer samples are relatively wider (about 2-3 μm) compared to the bilayer stripes (~ 1 μm) along the step edges in monolayer samples. This is likely due to the relatively higher growth temperature used for the growth of bilayer graphene, while the rest of the ambient conditions are quite similar.

2.3 Hydrogen intercalation

Thermal decomposition of the Si-face of SiC always leads to the formation of graphene-like carbon buffer layer at the interface of SiC and first graphene layer. The buffer layer is chemically bound to the substrate and therefore does not show graphene like properties. However, the bonding can be removed through hydrogen intercalation under certain conditions and the buffer layer can be transformed into an additional graphene layer. [31]. Hydrogen intercalation of the samples following the graphene growth process was performed in the temperature range of 1000-1100 K under a hydrogen background pressure of $5\text{-}6 \times 10^4$ Pa for 60 minutes without exposing the samples to air. In the case when graphene is directly grown on bare semi-insulating substrates, contactless measurements of charge carrier mobility, sheet carrier density and sheet resistance were estimated using microwave reflectivity at room temperature. The samples grown on bare semi-insulating substrates under similar conditions used for the growth of carbon buffer layer on homoepitaxial layer do not show any conductivity. After hydrogen intercalation, the samples became conductive with sheet resistance of about 200-400 $\Omega/\square$, a charge carrier density

of about $1 \times 10^{13} \text{ cm}^{-2}$ and a mobility of about $2000 \text{ cm}^2/\text{Vs}$. This confirms the formation of carbon buffer layer during the growth and its transformation into quasi-free-standing monolayer through hydrogen intercalation. The reference samples grown together with quasi-free-standing bilayer graphene samples showed relatively high values for mobility and charge carrier density $3000 \text{ cm}^2/\text{Vs}$ and $1.5 \times 10^{13} \text{ cm}^{-2}$, respectively and correspondingly low values of sheet resistance $150\text{-}300 \Omega/\square$, as measured by contactless measurements. These are averaged values obtained on large areas of several millimeters. The passivation of the SiC surface through hydrogen intercalation at the interface and conversion of carbon buffer layer into monolayer graphene are also confirmed by Raman spectra where much narrower G and 2D peaks are observed compared to as-grown graphene with carbon buffer layer present at the interface.

3. Graphene Characterization

Several characterization techniques were used to assess the graphene layers. The number of graphene layers was determined on random areas of the samples by reflectance mapping using a micro-Raman spectrometer. In case of graphene grown on semi-insulating substrate, the sheet resistance and the charge-carrier mobility were estimated using a contactless measurement technique. Van der Pauw structures were also fabricated in monolayer and bilayer graphene grown on homoepitaxial layers to access the electronic properties, and a comparison was made with graphene grown on bare substrates.

3.1 Reflectance and Raman mapping

The reflectance mapping as described in [32] is useful for obtaining direct information on the number of graphene layers on the investigated sample. Since the reflectance mapping alone is much faster than Raman mapping, it is used to map the graphene morphology (expressed in number of layers) on a relatively large area on the sample. Subsequent Raman mapping was performed on a chosen area within the larger reflectance map, thus yielding additional information on the stress conditions and the doping of the graphene. Since Raman and reflectance are compatible, another reflectance map is recorded during the Raman measurement in order to confirm that the same area within the larger reflectance map is repeated. Furthermore, each individual Raman spectrum can be labeled with the corresponding number of graphene layers.

Fig. 5 (a) Reflectance map on a sample with predominant monolayer graphene showing the number of graphene layers; (b) Reflectance map (left) taken on the outlined area of the larger map in part (a) of the figure together with the maps (right) of the peak positions and FWHM of the G- and 2D-peaks obtained from the Raman spectra; (c) The top spectrum represents the typical Raman spectra taken on the part of monolayer region with smaller line widths of the G- and 2D-peaks (the darker region in the FWHM maps in part (b) of the figure); the bottom spectrum is representative for the monolayer region with larger line widths (lighter region in the FWHM maps in part (b) of the figure).

Figs. 5 and 6 illustrate examples of reflectance and Raman maps of samples with predominantly monolayer (Fig.5) and bilayer (Fig.6) graphene together with typical Raman spectra obtained from the corresponding regions. In processing the Raman spectra of the monolayer, each of the G- and 2D-peaks is fitted with a single Lorentzian allowing for the rapid extraction of the peak positions and full widths at half maximum (FWHM) for each point on the map. In the case of bilayer or thicker graphene a single Lorentzian line is not appropriate for describing the line

shape of the 2D-peak due to the changed band structures in these more complicated systems. However, forcing a fit with a single Lorentzian still provides a reasonable estimation of the corresponding peak position and line width. In both figures, part (a) displays the larger reflectance map showing the number of graphene layers, with the region chosen for Raman-reflectance mapping is outlined. Part (b) in Fig 5b and Fig 6b display the maps built by color-coding the four parameters obtained from the fitting (peak position and FWHM of G- and 2D-peaks) together with the second reflectance map obtained simultaneously with the Raman mapping. Finally, in part (c) of each figure (Fig.5c and Fig.6c) typical Raman spectra from the corresponding regions are shown.

The reflectance map in Fig. 5 obtained in conjunction with the Raman mapping repeats the outlined area of the larger pure reflectance map of Fig. 5a. This area is chosen in advance for Raman mapping since it mainly contains quasi-free-standing monolayer graphene. Despite the homogeneity of the monolayer region as seen in reflectance, the positions of the G- and 2D-peaks from the Raman map displayed in Fig. 5b exhibit significant dispersion typical for graphene on SiC. This feature is typically interpreted in terms of the variation of mechanical stress conditions in the graphene layer. The assignment of the peak-position variations to stress variations in the graphene layer is also corroborated by the good correlation between the 2D- and G-peak positions (not shown). The G and 2D FWHM maps of the monolayer may qualitatively be divided into two regions which are well correlated. These two regions are seen as darker areas in the upper-left part and lighter in the lower-right part of the monolayer region in the FWHM maps for both 2D and G in Fig. 5b. The line broadening between these two areas is quite distinguished, from about $6 - 7 \text{ cm}^{-1}$ ($25 - 26 \text{ cm}^{-1}$) to approximately 9 cm^{-1} (29 cm^{-1}) for the G (2D) peak respectively. The reason for this segregation of the monolayer region is presently not understood. Such a clear segregation has not been observed previously in hydrogen intercalated samples grown directly on semi-insulating substrates. The observed change in the line widths is not likely to be due to change in the doping when moving from the one region to the other, because the G-peak shift associated with change in the doping [33] is not observed (cf. the spectra in Fig. 5c). Also, as seen from the peak-position maps in Fig. 5b, neither the G- nor 2D-peak positions are correlated with the different line widths in the two regions (cf. the peak-position maps in Fig. 5b). The D' peak at 1618 cm^{-1} which is associated with defect scattering is also present in the regions demonstrating broad G and 2D lines.

Fig. 6 (a) Reflectance spectrum on a larger (60 μm x 60 μm) area of sample with predominantly bilayer graphene. One-, two- and three-layer regions are observed as marked in the map. (b) The results from the simultaneous Raman-reflectance mapping on the area outlined in part (a), plotted in the same manner as in Fig. 4b. (c) The top three spectra picture the rather large variation of the peak positions of the G- and 2D-peaks on the bilayer region alone. The bottom spectrum is taken on one of the trilayer streaks and is given for comparison.

The reflectance map in Fig. 6a shows that although most of the surface is covered with bilayer, the morphology expressed in number of graphene layers is strongly influenced by the morphology of the underlying substrate (i.e. the CVD-grown epitaxial layers discussed previously). The spiral growth mode leads to the formation of relatively large hillocks possessing many larger steps on their slopes. A part of one such hillock is visible in the left part of the map in Fig. 6a. The area for Raman-reflectance mapping (outlined) was chosen away from the hillock in a region of the sample where presumably the step-flow growth mode has been effective. As was the case with the monolayer map, the reflectance map obtained together with the Raman

measurement essentially repeat the outlined region in Fig.6a. However, unlike the case of monolayer graphene, the maps of the four Raman parameters show much more dispersion in both the peak positions and line widths of G- and 2D-peaks. The spectra change quite abruptly between neighboring points on the map despite the fact that the laser spot (~ 700 nm) is larger than the pitch of the map (300 nm). This indicates an inhomogeneous stress distribution which manifests on a microscopic scale (smaller than the laser spot). Many spectra exhibit split of the G-peak into two components (not shown), which also suggests large stress variations on a microscopic scale. These variations are likely due to the rougher morphology of this bilayer sample. The upper three spectra in Fig.6c illustrate the large variation of the peak positions on the bilayer region alone (about 7 cm^{-1} and 15 cm^{-1} for the G- and 2D-peaks, respectively). The bottom spectrum taken on one of the trilayer inclusions is also displayed for comparison. Monolayer inclusions are also encountered in few points, also confirmed by the corresponding Raman spectra (not shown). These inclusions are visible also in the large reflectance map (cf. Fig. 6a).

3.2 Electrical characterization

Several $100\text{ }\mu\text{m}^2$ Van der Pauw structures are fabricated on graphene grown on both SI SiC substrates and on n-type homoepitaxial layers of SiC [34]. Measurements of the Hall properties of these structures yield valuable information about the uniformity of the electron transport properties in large area epitaxial graphene layers. The fabrication of the Hall structures is performed using an in-house process optimized for epitaxial graphene. The process begins by the deposition of a 10 nm passivation layer of Al_2O_3 in several steps. In each step 1.5 nm of Aluminum metal is deposited over the graphene layer and subsequently oxidized at 453 K [35]. The purpose of this passivation layer is to protect the native graphene layers from further process environments. Although the Al_2O_3 layer is amorphous due to the deposition method, it serves quite well as an initial passivation layer.

Following the patterning of alignment marks, Ohmic contacts are patterned using photolithography. The thin passivation layer is then etched in a weak solution of 1:10 HF:DI. Following etching, a metal stack of 10/10/40 nm of Ti/Pt/Au is deposited in order to form Ohmic contacts to the graphene layers. Next, mesa isolation is performed by patterning via photolithography and ICP etching in Cl_2/Ar plasma at 400 W for 30s. Alternatively, the mesa

isolation can be achieved by wet etching the Al_2O_3 in dilute HF and etching the graphene in O_2 plasma at 50 W for 30s. The first method is found to be desirable as the HF solution has a tendency to corrode the Ti layer of the contact metallization thus degrading the contact quality. Finally, the Ohmic contacts are extended onto the SiC substrate via photolithography and evaporation of a 10/100/10 nm stack of Ti/Au/Ti. The first Ti layer serves to glue the contact to the substrate, while the final Ti layer aids in liftoff. This final step is necessary as the adhesion of Ti to graphene is generally found to be quite poor. Electrical characterization of the fabricated Van der Pauw structures is performed in a Biorad HL5500PC Hall system. The carrier mobility and sheet resistance are plotted as a function of carrier density for several samples. For the measurements of graphene grown on the homoepitaxial SiC, the sheet resistance of the epitaxial layer is very high compared with that of the graphene. For this reason, it can be assumed that the measured Hall voltage will be almost entirely due to current carried by the graphene layers. The influence of the conductivity of the homoepitaxial SiC layers on Hall measurements is assumed to be minimal.

Monolayers and bilayers grown on epitaxial SiC layers are compared to a typical monolayer sample grown directly on the SI SiC substrate. The measurements are carried out at 300 K, and each data point represents a measurement of a separate Hall structure. On each $16 \times 16 \text{ mm}^2$ chip, 48 structures are measured; only structures with high symmetry in the Hall voltage indicating a reliable measurement are reported. The results are summarized in Fig 7.

Several Hall structures on three $16 \times 16 \text{ mm}^2$ samples are measured: monolayer on SI substrate, monolayer on epitaxial SiC, and bilayer on epitaxial SiC. The epilayers demonstrate several divergences from monolayer on SI substrate. First, it should be noted that the monolayer on SI substrate exhibits a fairly constant carrier density of $1 \times 10^{13} \text{ cm}^{-2}$. The mobility of this monolayer sample is of order $1500\text{--}2500 \text{ cm}^2/\text{V}\cdot\text{s}$ and its sheet resistance varies on the order of $200\text{--}400 \Omega/\square$. Such values are typical of epitaxial graphene grown on SiC after processing. Furthermore, the sample is uniformly p-type which is expected from hydrogen intercalation [31, 36]. Overall, the SI SiC control represents a high quality control by which to gauge the overall electrical characteristics of epitaxial graphene grown on SiC epi-layers.

For the monolayer on epitaxial SiC, the Hall data forms a very tight cluster of points with an average mobility on the order of $800 \text{ cm}^2/\text{V}\cdot\text{s}$. Furthermore, the carrier density observed is very high when compared to the SI control sample however, the origin of this high carrier density is

Fig. 7 Scatter plots of the Hall mobility (a) and sheet resistance (b) as a function of carrier density for several samples included in this study. Each data point represents a measurement taken on a single Hall structure. Several Hall structures on three $16 \times 16 \text{ mm}^2$ samples are measured: monolayer on SI, monolayer on homoepitaxial SiC layer, and bilayer on homoepitaxial SiC layer.

currently unknown. On the other hand, the graphene monolayer on epitaxial SiC demonstrates exemplary uniformity in terms of its electron transport characteristics. This uniformity is thought to be reflective of the underlying uniformity of the SiC epitaxial layers that is observed after monolayer growth (Fig. 4).

The results for bilayers grown on epitaxial SiC are equally interesting. A very wide dispersion in the mobility, sheet resistance and carrier density appears in the Hall measurements. The mobility, sheet resistance and carrier density vary from $700\text{--}2300 \text{ cm}^2/\text{V} \cdot \text{s}$, $200\text{--}500 \Omega/\square$, and $0.85\text{--}1.3 \times 10^{13} \text{ cm}^{-2}$ respectively. Of these figures, the variation in the carrier density is perhaps the most relevant as it implies a wide variation in the Fermi energy at various points in the bilayer sample. In particular, the measurement of $0.85 \times 10^{13} \text{ cm}^{-2}$ suggests a Fermi energy of 150 meV. A device fabricated on material of such low doping would likely exhibit a high capability for modulation as the Fermi energy is somewhat near to the point of minimum conduction. It should be noted that this particular structure also exhibits a respectable carrier mobility of about $2000 \text{ cm}^2/\text{V} \cdot \text{s}$ and a sheet resistance of $360 \Omega/\square$. The bilayer sample also has many structures which demonstrate very high carrier density which are not suitable for a device oriented application. Perhaps the most striking feature is the lack of uniformity in the electron transport

characteristics of the bilayer sample. This reflects the observation that the epitaxial SiC layers become more disordered after bilayer growth than after monolayer growth (i.e. that disorder in the graphene layers is reflective of the substrate surface properties). The average carrier density of the bilayer on epitaxial SiC sample is on the order of $1.1 \times 10^{13} \text{ cm}^{-2}$, which is very typical of H-intercalated bilayers on SI SiC.

In general, the electron transport characteristics measured on the graphene on homoepitaxial SiC layers are quite positive for this preliminary experiment as the results conform relatively well with what is observed on graphene grown on SI SiC samples [34]. Furthermore, all structures were found to be p-type suggesting that hydrogen intercalation was successful. Also, the transport measurements after fabrication correlate well with microwave reflectivity measurements taken prior to fabrication indicating that the graphene layers are not substantially altered by processing. These results suggest a compatibility between graphene growth and epitaxial n-type SiC which is positive from the perspective of electron devices in graphene.

4. Discussion

The surface morphology of on-axis homoepitaxial layers is highly influenced by the growth mechanism, and the growth mechanism is mainly controlled by the off-cut of the substrate under certain growth conditions. However, on nominally on-axis substrate with an off-cut of less than 0.1° , the growth mechanism can be controlled by tuning the C/Si ratio. Spiral growth dominates in carbon rich conditions, while step-flow growth dominates in silicon rich conditions [37]. By tuning to a silicon rich environment, it is possible to limit the growth mode to step-flow growth thereby obtaining well-arranged large steps on the surface with very wide terraces. However, in this work homoepitaxial layers were grown at C/Si ratio of 1 in order to obtain high nitrogen doping at low flow rate of nitrogen.

The epilayer surface appears to be relatively rougher compared to the substrate surface exposed to similar temperature under hydrogen ambient. This is mainly due to heavy step-bunching during homoepitaxial growth on the Si-face along with a mixture of different growth mechanism on the on-axis substrate. However, it is possible to further optimize the growth process to reduce the surface roughness. As-grown epilayer surfaces consist of relatively wide regions covered with small steps of 0.5 to 1 nm height between large steps of few tens of nm height. The large steps are usually not steep and extend over very large area (several tens of

microns) on the surface. This morphology is advantageous in the context of graphene growth when compared to steep steps formed on the substrate during surface preparation in hydrogen ambient. Steep edges usually show uncontrolled growth of multilayer graphene which may significantly influence the electrical properties of devices made in such material. Also the atomically flat terraces on epilayer surface are much wider compared to the substrate surface etched in hydrogen under similar temperatures. Under controlled growth conditions, wide terraces lead to the formation of uniform thickness of graphene over large areas only limited by the width of the terraces.

The number of graphene layers and thickness uniformity is found to be extremely sensitive to the growth temperature and ambient conditions. Although the temperature distribution in the region of the susceptor ($75 \times 75 \text{ mm}^2$) used for samples is within $\pm 10 \text{ K}$, a considerable variation has been observed in the thickness uniformity among different samples grown during the same growth run. The measured temperature distribution was observed under heavy hydrogen flow at a pressure of 20 kPa . However, the pressure used for graphene growth is around $1 \times 10^{-3} \text{ Pa}$. These low pressures may significantly influence temperature distribution in the susceptor. The graphene thickness variations are generally high among the samples placed along the length of the susceptor which is most probably due to inhomogeneous ambient conditions and temperature gradient along the length of susceptor. A comparison of reflection maps (not shown), taken from the sample placed in the upstream side of the susceptor showed considerably more uniform graphene thickness compared to the samples placed at the downstream side of the susceptor. Considering the monolayer graphene samples, large areas without graphene formation are observed in the samples placed towards the downstream side of the susceptor. This clearly indicates a relatively lower temperature and higher Si background pressure at the downstream side of the susceptor. These observations manifest the importance of both the uniformity of temperature and the Si background pressure on graphene uniformity.

It is well known that higher preferential removal rate of Si from larger steps leads to the formation of multiple layer of graphene on step edges. The height of large steps formed on the epilayer surface is much greater compared to the steps formed on the substrate surface during in-situ surface etching. However, the stripes of bilayer/trilayer graphene visible along the edges in the samples containing mainly monolayer/bilayer graphene are very narrow. This shows that a more homogeneous removal rate of Si can be maintained under Si-rich environment and high

thickness uniformity of graphene can be obtained over large areas. Similar behavior was observed in the case of monolayer and bilayer graphene growth directly on the substrate under Si background pressure (the reference samples).

When the growth is optimized for only the carbon buffer layer, step edges demonstrate both buffer layer and monolayer graphene. This suggests that nucleation of graphene starts at the step edges in the form of a C-buffer layer and then proceeds towards the smoother regions of the substrate. Under precisely controlled temperature and Si background pressure, the nucleation process can be limited to the formation of C-buffer layer. However, this may lead to incomplete coverage of the substrate. Our growth process was optimized to obtain complete coverage of C-buffer layer which also lead to the formation of additional graphene layer at the step edges.

The background pressure during graphene growth plays a critical role at relatively high temperature. The temperature of the phase transition at the surface between Si-rich to C-rich can be increased by at least a few hundred Kelvin by just increasing the background pressure. A relatively high background pressure also widens the window for graphene growth in the context of temperature allowing for the tuning the growth process to avoid preferential evaporation of Si at the step edges. This in turn allows one to overcome the limits on thickness uniformity posed by the preferential high evaporation rate of Si at the step edges.

Successful intercalation of hydrogen is also evident from the narrowing of the G- and 2D-peaks in the case of monolayer graphene compared to as-grown graphene with C-buffer layer present at the interface. As-grown monolayer graphene with carbon buffer layer usually displays broader peaks with FWHM larger than 10 cm^{-1} (34 cm^{-1}) for the G (2D) peak. However, when the monolayer is obtained by conversion of the carbon buffer layer in graphene the typical G and 2D peak FWHMs are in the ranges $5\text{-}10\text{ cm}^{-1}$ and $20\text{-}30\text{ cm}^{-1}$, respectively. In this case, the narrowing of the G-peak is associated with the increased doping as discussed before.

The surface morphologies of monolayer and bilayer graphene as observed by optical microscopy are quite similar. AFM characterization revealed a rougher surface on the bilayer sample. This increase in surface roughness was expected due to a relatively high growth temperature. The large steps are relatively higher compared to those in monolayer graphene samples and the structure of smaller steps is similar to the monolayer case. High surface roughness leads to a non-uniform sublimation rate and enhances the possibility of thickness non-uniformities which is confirmed by reflectance and Raman mappings. The Raman maps also

provide evidence for inhomogeneous surface morphology of bilayer graphene compared to the case of monolayer graphene, which leads to the scattered stress distribution observed in bilayers. Large area reflectance maps of monolayer and bilayer samples (Fig. 5 and 6) show different distributions of thicknesses of monolayer and bilayer graphene, respectively. In samples grown intentionally as monolayer graphene, only stripes of bilayer graphene on step edges are observed while monolayer graphene is formed on wide terraces. On the other hand, in the case of bilayer graphene, inclusions of monolayer graphene are also formed on some of the wide terraces together with trilayer graphene on step edges. Although, it is possible to eliminate these monolayer inclusions by increasing the growth temperature, an accompanying extension of the trilayer regions onto terraces is also observed. This indicates much narrower growth window for bilayer graphene compared to monolayer graphene, and the presence of steps on the surface makes the bilayer growth much more difficult than monolayer.

The surface morphology of graphene grown on a bare substrate is substantially different from the graphene on homoepitaxial layers (Fig.3c and e). A more linear surface step structure with relatively narrow terraces is observed in these samples. Also, no large steps with irregular pattern are observed in samples on bare substrates. The corresponding reflectance and Raman maps (not shown) also reproduce similar structure in the form of non-uniform distribution of the thickness of graphene. A comparison of reflectance maps and Raman maps of graphene grown on homoepitaxial layers and on bare substrates reveals that the thickness uniformity of graphene is much better on homoepitaxial layers. Also, the growth window for monolayer graphene is wider compared to bilayer graphene making it easier to obtain large area monolayer graphene.

Measurements of the room temperature electron transport properties of graphene monolayers and bilayers grown on epitaxial SiC conform somewhat well to the properties of graphene layers grown directly on SI SiC substrates. All of the hydrogen intercalated samples measured were observed to be uniformly p-type. The monolayers on epi-SiC demonstrate a mobility of order $800 \text{ cm}^2/\text{Vs}$ and a high carrier density of $1.5 \times 10^{13} \text{ cm}^{-2}$. Furthermore, the monolayers are highly uniform with regard to their transport characteristics. Bilayers on epi-SiC demonstrate a much wider range of mobilities ($700\text{-}2300 \text{ cm}^2/\text{Vs}$) and carrier densities ($0.85\text{-}1.3 \text{ cm}^{-2}$). This suggests that transport properties in graphene bilayers grown on epitaxial SiC inherit the non-uniformity observed in AFM and Raman measurements of graphene bilayers. Furthermore, the bilayer sample exhibits regions of high mobility ($>2000 \text{ cm}^2/\text{Vs}$) and low carrier density ($<0.9 \times 10^{13} \text{ cm}^{-2}$).

²). Such regions are not demonstrated by bilayer counterparts grown directly on SI SiC substrates. The inhomogeneities of graphene transport properties in bilayer graphene on epilayer reflect, in part, that of the SiC surface morphology. The large surface steps in bilayer graphene on epilayer are regarded as the sources of the degradation of mobility in epitaxial graphene and leads to large variations in mobility across the sample. This observation is consistent with several other recent investigations showing a correlation between macroscopic electrical measurements and surface morphology [38-40]. If these properties could be uniformly achieved over large areas, then bilayers grown on epitaxial SiC layers could offer a substantial improvement to the current technique of graphene grown directly on SI SiC substrates in the context of a device oriented application. Further efforts will be directed towards optimizing the growth of hydrogen intercalated graphene bilayers on epitaxial SiC with the aim of achieving uniformly high mobility and low carrier density.

5. Summary

Quasi-free standing monolayer and bilayer graphene is grown on n-type doped ($1 \times 10^{16} \text{ cm}^{-3}$) on-axis homoepitaxial layers of 4H-SiC. Homoepitaxial layers with 100% 4H polytype were grown using an optimized on-axis growth process. Graphene growth was made in controlled Si background pressure. In order to obtain monolayer graphene only carbon buffer layer was grown whereas for bilayer graphene, monolayer graphene was grown on homoepitaxial layers. The hydrogen intercalation process was used to convert carbon buffer layer into monolayer and monolayer into bilayer graphene. Micro-Raman and reflectance mappings confirmed predominant quasi-free-standing monolayer and bilayer graphene on samples grown under optimized growth conditions. Van der Pauw structures are fabricated in these layers using photolithography. Bilayer samples show relatively high values of charge carrier mobility ($>2000 \text{ cm}^2/\text{Vs}$) and low carrier density ($<0.9 \times 10^{13} \text{ cm}^{-2}$) compared to monolayers on homoepitaxial layers with charge carrier mobility of ($800 \text{ cm}^2/\text{Vs}$) and high carrier density ($1.5 \times 10^{13} \text{ cm}^{-2}$). Furthermore, bilayers on homoepitaxial layers are also superior in quality compared to bilayers grown directly on SI substrates.

Acknowledgements

This work was supported by the European Science Foundation (ESF) under the EUROCORES Program EuroGRAPHENE and Swedish Research Councils (VR) as well as the Swedish Government Strategic Research Area Grant in Materials Science.

References

- [1] J.S. Moon, D. Curtis, M. Hu, D. Wong, C. McGuire, P.M. Campbell, G. Jernigan, J.L. Tedesco, B. VanMil, R. Myers-Ward, C. Eddy, Jr., D.K. Gaskill, Epitaxial-graphene RF field-effect transistors on Si-face 6H-SiC substrates, *Ieee Electr Device L*, 30 (2009) 650-652.
- [2] Y.Q. Wu, P.D. Ye, M.A. Capano, Y. Xuan, Y. Sui, M. Qi, J.A. Cooper, T. Shen, D. Pandey, G. Prakash, R. Reifenger, Top-gated graphene field-effect-transistors formed by decomposition of SiC, *Appl Phys Lett*, 92 (2008).
- [3] J. Kedzierski, P.L. Hsu, P. Healey, P.W. Wyatt, C.L. Keast, M. Sprinkle, C. Berger, W.A. de Heer, Epitaxial graphene transistors on SiC substrates, *Ieee T Electron Dev*, 55 (2008) 2078-2085.
- [4] F. Schwierz, Graphene transistors, *Nat Nanotechnol*, 5 (2010) 487-496.
- [5] J.S. Moon, D. Curtis, S. Bui, M. Hu, D.K. Gaskill, J.L. Tedesco, P. Asbeck, G.G. Jernigan, B.L. VanMil, R.L. Myers-Ward, C.R. Eddy, P.M. Campbell, X. Weng, Top-Gated Epitaxial Graphene FETs on Si-Face SiC Wafers With a Peak Transconductance of 600 mS/mm, *Ieee Electr Device L*, 31 (2010) 260-262.
- [6] G. Gu, S. Nie, R.M. Feenstra, R.P. Devaty, W.J. Choyke, W.K. Chan, M.G. Kane, Field effect in epitaxial graphene on a silicon carbide substrate, *Appl Phys Lett*, 90 (2007).
- [7] C. Virojanadara, M. Syväjarvi, R. Yakimova, L.I. Johansson, A.A. Zakharov, T. Balasubramanian, Homogeneous large-area graphene layer growth on 6H-SiC(0001), *Phys Rev B*, 78 (2008) 245403.
- [8] K.V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G.L. Kellogg, L. Ley, J.L. McChesney, T. Ohta, S.A. Reshanov, J. Rohrl, E. Rotenberg, A.K. Schmid, D. Waldmann, H.B. Weber, T. Seyller, Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide, *Nature Materials*, 8 (2009) 203-207.
- [9] R. Tromp, J. Hannon, Thermodynamics and kinetics of graphene growth on SiC (0001), *Phys Rev Lett*, 102 (2009) 106104.
- [10] P. Sutter, EPITAXIAL GRAPHENE How silicon leaves the scene, *Nature Materials*, 8 (2009) 171-172.
- [11] W.A. de Heer, C. Berger, M. Ruan, M. Sprinkle, X.B. Li, Y.K. Hu, B.Q. Zhang, J. Hankinson, E. Conrad, Large area and structured epitaxial graphene produced by confinement controlled sublimation of silicon carbide, *P Natl Acad Sci USA*, 108 (2011) 16900-16905.
- [12] S.V. A. Michon, A. Ouerghi, M. Zielinski, T. Chassagne, and M. Portail, Direct growth of few-layer graphene on 6H-SiC and 3C-SiC/Si via propane chemical vapor deposition, *Appl Phys Lett*, 97 (2010).

- [13] W. Strupinski, K. Grodecki, A. Wyszomolek, R. Stepniewski, T. Szkopek, P.E. Gaskell, A. Gruneis, D. Haberer, R. Bozek, J. Krupka, J.M. Baranowski, Graphene Epitaxy by Chemical Vapor Deposition on SiC, *Nano Lett*, 11 (2011) 1786-1791.
- [14] X.S. Li, W.W. Cai, J.H. An, S. Kim, J. Nah, D.X. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S.K. Banerjee, L. Colombo, R.S. Ruoff, Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils, *Science*, 324 (2009) 1312-1314.
- [15] K.S. Kim, Y. Zhao, H. Jang, S.Y. Lee, J.M. Kim, K.S. Kim, J.H. Ahn, P. Kim, J.Y. Choi, B.H. Hong, Large-scale pattern growth of graphene films for stretchable transparent electrodes, *Nature*, 457 (2009) 706-710.
- [16] P.W. Sutter, J.I. Flege, E.A. Sutter, Epitaxial graphene on ruthenium, *Nature Materials*, 7 (2008) 406-411.
- [17] X.S. Li, Y.W. Zhu, W.W. Cai, M. Borysiak, B.Y. Han, D. Chen, R.D. Piner, L. Colombo, R.S. Ruoff, Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes, *Nano Lett*, 9 (2009) 4359-4363.
- [18] Q.K. Yu, J. Lian, S. Siriponglert, H. Li, Y.P. Chen, S.S. Pei, Graphene segregated on Ni surfaces and transferred to insulators, *Appl Phys Lett*, 93 (2008).
- [19] E.V. Castro, K.S. Novoselov, S.V. Morozov, N.M.R. Peres, J.M.B.L. Dos Santos, J. Nilsson, F. Guinea, A.K. Geim, A.H.C. Neto, Biased bilayer graphene: Semiconductor with a gap tunable by the electric field effect, *Phys Rev Lett*, 99 (2007) -.
- [20] Y.B. Zhang, T.T. Tang, C. Girit, Z. Hao, M.C. Martin, A. Zettl, M.F. Crommie, Y.R. Shen, F. Wang, Direct observation of a widely tunable bandgap in bilayer graphene, *Nature*, 459 (2009) 820-823.
- [21] K.F. Mak, C.H. Lui, J. Shan, T.F. Heinz, Observation of an Electric-Field-Induced Band Gap in Bilayer Graphene by Infrared Spectroscopy, *Phys Rev Lett*, 102 (2009).
- [22] S. Tanabe, Y. Sekine, H. Kageshima, M. Nagase, H. Hibino, Observation of Band Gap in Epitaxial Bilayer Graphene Field Effect Transistors, *Jpn J Appl Phys*, 50 (2011).
- [23] S.Y. Zhou, G.H. Gweon, A.V. Fedorov, P.N. First, W.A. De Heer, D.H. Lee, F. Guinea, A.H.C. Neto, A. Lanzara, Substrate-induced bandgap opening in epitaxial graphene., *Nature Materials*, 6 (2007) 916-916.
- [24] J. Hassan, J.P. Bergman, A. Henry, E. Janzen, On-axis homoepitaxial growth on Si-face 4H-SiC substrates, *J Cryst Growth*, 310 (2008) 4424-4429.
- [25] J. Hassan, J.P. Bergman, A. Henry, E. Janzen, In-situ surface preparation of nominally on-axis 4H-SiC substrates, *J Cryst Growth*, 310 (2008) 4430-4437.
- [26] J. Hassan, J.P. Bergman, A. Henry, E. Janzen, High growth rate with reduced surface roughness during on-axis homoepitaxial growth of 4H-SiC, *Mat. Sci. Forum*, 679-680 (2011) 115-118.

- [27] C. Riedl, A.A. Zakharov, U. Starke, Precise insitu thickness analysis of epitaxial graphene layers on SiC(0001) using low-energy electron diffraction and angle resolved ultraviolet photoelectron spectroscopy, *Appl Phys Lett*, 93 (2008) 033106-033101.
- [28] J. Robinson, X.J. Weng, K. Trumbull, R. Cavaleiro, M. Wetherington, E. Frantz, M. LaBella, Z. Hughes, M. Fanton, D. Snyder, Nucleation of Epitaxial Graphene on SiC(0001), *Acs Nano*, 4 (2010) 153-158.
- [29] J. Hassan, C. Virojanadara, A. Meyer, I.G. Ivanov, J.I. Flege, S. Watcharinyanon, J. Falta, L.I. Johansson, E. Janzen, Control of epitaxial graphene thickness on 4H-SiC(0001) and buffer layer removal through hydrogen intercalation, *Silicon Carbide and Related Materials 2011*, Pts 1 and 2, 717-720 (2012) 605-608.
- [30] J. Ul Hassan, A. Meyer, S. Cakmakyapan, O. Kazar, J.I. Flege, J. Falta, E. Ozbay, E. Janzen, Surface evolution of 4H-SiC(0001) during in-situ surface preparation and its influence on graphene properties, *Silicon Carbide and Related Materials 2012*, 740-742 (2013) 157-160.
- [31] C. Riedl, C. Coletti, T. Iwasaki, A.A. Zakharov, U. Starke, Quasi-Free-Standing Epitaxial Graphene on SiC Obtained by Hydrogen Intercalation, *Phys Rev Lett*, 103 (2009).
- [32] I.G. Ivanov, J. Ul Hassan, T. Iakimov, A.A. Zakharov, R. Yakimova, and E. Jánzén, Layer-Number Determination in Graphene on SiC by Reflectance Mapping, *Carbon*, 77 (2014) 492-500.
- [33] J. Yan, Y.B. Zhang, P. Kim, A. Pinczuk, Electric field effect tuning of electron-phonon coupling in graphene, *Phys Rev Lett*, 98 (2007).
- [34] M. Winters, J. Hassan, H. Zirath, E. Janzen, N. Rorsman, A temperature dependent measurement of the carrier velocity vs. electric field characteristic for as-grown and H-intercalated epitaxial graphene on SiC, *J Appl Phys*, 113 (2013).
- [35] S. Kim, J. Nah, I. Jo, D. Shahrjerdi, L. Colombo, Z. Yao, E. Tutuc, S.K. Banerjee, Realization of a high mobility dual-gated graphene field-effect transistor with Al₂O₃ dielectric, *Appl Phys Lett*, 94 (2009).
- [36] C. Riedl, C. Coletti, U. Starke, Structural and electronic properties of epitaxial graphene on SiC(0001): a review of growth, characterization, transfer doping and hydrogen intercalation, *J Phys D Appl Phys*, 43 (2010).
- [37] J. Ul Hassan, I. Booker, L. Lilja, A. Hallen, M. Fagerlind, P. Bergman, E. Janzen, On-axis homoepitaxial growth of 4H-SiC PiN structure for high power applications, *Silicon Carbide and Related Materials 2012*, 740-742 (2013) 173-176.
- [38] M.K. Yakes, D. Gunlycke, J.L. Tedesco, P.M. Campbell, R.L. Myers-Ward, C.R. Eddy, D.K. Gaskill, P.E. Sheehan, A.R. Laracuente, Conductance Anisotropy in Epitaxial Graphene Sheets Generated by Substrate Interactions, *Nano Lett*, 10 (2010) 1559-1562.
- [39] S.H. Ji, J.B. Hannon, R.M. Tromp, V. Perebeinos, J. Tersoff, F.M. Ross, Atomic-scale transport in epitaxial graphene, *Nature Materials*, 11 (2012) 114-119.
- [40] G. Nicotra, Q.M. Ramasse, I. Deretzis, A. La Magna, C. Spinella, F. Giannazzo, Delaminated Graphene at Silicon Carbide Facets: Atomic Scale Imaging and Spectroscopy, *Acs Nano*, 7 (2013) 3045-3052.