Multi-scale investigations of interface properties, stacking order and decoupling of few layer graphene on C-face 4H-SiC

C. Bouhafs^{a,*}, A. A. Zakharov^b, I. G. Ivanov^c, F. Giannazzo^d, J. Eriksson^c,
V. Stanishev^a, P. Kühne^a, T. Iakimov^c, T. Hofmann^e, M. Schubert^e, F.
Roccaforte^d, R. Yakimova^c, V. Darakcheiva^a

^a*Terahertz Materials Analysis Center, Department of Physics, Chemistry and Biology,
IFM, Linköping University, Linköping S-58183 SE, Sweden*

^b*MaxLab, Lund University, S-22100 Lund, Sweden*

^c*Department of Physics, Chemistry and Biology, IFM, Linköping University, Linköping
S-58183 SE, Sweden*

^d*CNR-IMM, Strada VIII, 5, 95121 Catania, Italy*

^e*Department of Electrical Engineering and Center for Nanohybrid Functional Materials,
University of Nebraska-Lincoln, Lincoln, Nebraska 68588, U.S.A*

Abstract

In this work, we report a multi-scale investigation using several nano-, micro and macro- scale techniques of few layer graphene (FLG) sample consisting of large monolayer (ML) and bilayer (BL) areas grown on C-face 4H-SiC (000-1) by high-temperature sublimation. Single 1×1 diffraction patterns are observed by micro-low-energy electron diffraction for ML, BL and tri-layer graphene with no indication of out-of-plane rotational disorder. A SiO_x layer is identified between graphene and SiC by X-ray photoelectron emission spectroscopy and reflectance measurements. The chemical composition of the interface layer changes towards SiO_2 and its thickness increases with aging in normal ambient conditions. The formation mechanism of the inter-

*Corresponding author: Tel: 0046 13 285707. E-mail: vanya.darakchieva@liu.se

face layer is discussed. It is shown by torsion resonance conductive atomic force microscopy that the interface layer causes the formation of non-ideal Schottky contact between ML graphene and SiC. This is attributed to the presence of a large density of interface states. Mid-infrared optical Hall effect measurements revealed Landau-level transitions in FLG that have a square-root dependence on magnetic field, which evidences a stack of decoupled graphene sheets. Contrary to previous works on decoupled C-face graphene, our BL and FLG are composed of ordered decoupled graphene layers without out-of-plane rotation.

1. Introduction

Graphene grown by sublimation on silicon carbide (SiC) offers a viable route towards production of large-scale electronic grade single-crystalline material on semi-insulating (SI) substrate without the need of transfer [1, 2, 3, 4, 5, 6]. In particular, graphene grown on the C-face ($000\bar{1}$) of 4H- and 6H-SiC (C-face graphene) presents interest due to its high mobility parameters as compared to Si-face graphene (grown on the (0001) surface of 4H-, 6H-SiC) [7, 8, 9, 10, 11, 12]. C-face graphene with free charge carrier mobility in the range of 5000 - 18000 cm^2/Vs at room temperature has been demonstrated [8, 11, 12], which raises the hope to achieve epitaxial material with electronic properties matching those of exfoliated graphene transferred on either SiO_2/Si [13] or BN [14]. On the other hand, the room-temperature mobility parameters of Si-face graphene are significantly lower, 900-2400 cm^2/Vs for as-grown [7, 9] and up to 3100 cm^2/Vs for hydrogen intercalated quasi-free-standing graphene [15].

In contrast to Si-face graphene, which is extensively studied and well understood, the interface and structural properties of C-face graphene are not established. In all Si-face graphene, a buffer layer with $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ surface reconstruction surface is always found at the interface with SiC independently of growth temperature, environment, pressure, number of layers etc. [16, 17]. The buffer layer has a graphene-like arrangement with mixed sp^3 - sp^2 hybridization and it is strongly bonded to the substrate [16, 17]. On the other hand, very different interface properties and surface reconstructions are reported for C-face graphene although it is generally accepted that it is weakly bonded to the substrate [18, 19]. For C-face graphene grown at relatively low temperatures (up to 1400°C) in ultra-high vacuum, coexistence of 2×2 and 3×3 SiC surface reconstructions are reported for low graphene coverage [16, 19]. When grown at slightly higher temperatures of 1475°C and in Ar atmosphere 1×1 surface reconstruction [20] or a disordered interface [21] are observed. Mathieu *et al.* reported chemically heterogeneous interface layer for such graphene samples with at least two different SiC surface chemical states [20]. As a result, a local variation of C-face graphene workfunction was observed and attributed to different charge transfer from each of the SiC interfaces [20].

For C-face graphene grown by high-temperature sublimation in Ar atmosphere (1850°C - 2000°C) no specific SiC surface reconstruction has been reported [22]. We have recently shown that an amorphous layer consisting of a mixture of C and Si is formed between graphene and SiC for high-temperature growth in Ar atmosphere on mechanically polished 4H-SiC [23]. The thickness of the interface layer was shown to increase with increasing

growth temperature and number of graphene layers [23]. The presence of an amorphous interface layer containing Si, C and O was also reported for a similar C-face graphene sample grown by high-temperature sublimation in Ar [24]. In this case, the interface layer had a constant thickness independent of graphene number of layers. For electronic device applications typically high-purity SiC substrates with chemically-mechanically polished (epi-ready) surfaces should be employed. Whether an interface layer would also occur in the case of C-face graphene grown on epi-ready surfaces of SiC without polishing defects is not known. The properties of the interface layer will have critical implications for the performance of C-face graphene devices. Despite the numerous reports, very little is known about the effect of the interface layer on the electronic, transport and structural properties of C-face graphene.

In addition, there is an ongoing controversy about the nature of C-face graphene grown in Ar at relatively high temperatures [22, 21, 25]. It has been argued that a rotational disorder between the layers in few-layer graphene (FLG) stack leads to their decoupling, which can provide an explanation for the single π -band observed for C-face FLG in angle-resolved photoemission spectroscopy (ARPES) [18, 21]. On the other hand, Johansson et al. reported that rotation of different domains does not occur out-of-plane between adjacent layers in the stack when graphene is grown at high temperature, but rather in-plane within the same graphene sheet [22]. However, it was not clear if these ordered graphene sheets were decoupled or not. Recently, it was reported by nano-ARPES that C-face graphene grown at high temperature in Ar atmosphere is AB stacked and the single π -band observed in

ARPES experiments is a superposition of several multiple bands associated with two, three or more AB stacked layers [25]. The reasons behind decoupling of individual sheets in C-face graphene are not well understood and present an important scientific question from fundamental and technological points of view. The (de)coupling of C-face graphene also has crucial impact on its electronic properties and applications in electronic device. A stack of decoupled graphene sheets exhibits a Dirac-like band structure with linearly dispersing bands (Dirac cones) at the graphene K point, and free-charge carriers behave as massless Dirac fermions. In such a case, special transport properties arise from the chiral nature of free charge carriers leading to extremely high mobility parameters, ballistic transport, linear current-voltage characteristics, reduced back-scattering, electric field effect, anomalous quantum Hall effect, etc. On the other hand, a stack of coupled graphene layers exhibits a parabolic band structure with massive free charge carriers.

In this work, we investigate the interface properties, stacking order and decoupling of C-face graphene with large homogeneous areas of monolayer (ML), bi-layer (BL) and tree-layer (TL) grown by high-temperature sublimation (1950°C) on 4H-SiC. C-face graphene is a complex material and consists typically of multi-layer domains with varying thicknesses and/or properties, e.g. stacking order, doping, decoupling [26, 27]. Consequently, a multi-scale approach combining advanced experimental characterizations tools is needed to properly investigate and understand the properties of C-face graphene. We have combined several nanoscale (low-energy electron microscopy, X-ray photo-electron emission microscopy, scanning Kelvin probe microscopy, torsion conductive atomic force microscopy), microscale (low-energy electron

diffraction, X-ray photo-electron spectroscopy, Raman scattering, reflectance mapping and linescan measurements) and macroscopic (mid-infrared optical Hall effect) characterization techniques to investigate the effect of the interface layer on the electrical properties and doping of graphene in correlation
 95 with the number of graphene layers and their stacking order. A SiO_x layer is identified at the interface between graphene and SiC independently of graphene thickness and domain size. The evolution of the interface layer properties with graphene aging at normal ambient conditions is investigated. Special focus is put on the effect of interface layer on the contact behavior
 100 for electrical transport between ML graphene and SiC. Doping and defects of graphene in relation to number of graphene layers is discussed in detail. Finally, the coupling of individual graphene sheets in BL and FLG is investigated and discussed.

2. Experimental details

105 An inductively heated furnace was used for the high-temperature sublimation of graphene under high isothermal conditions [28]. Graphene was grown at 1950°C on the C-terminated surface of a high purity semi-insulating nominally on-axis 4H-SiC(000 $\bar{1}$) substrate (CREE, Inc.) in Ar at pressure of 1 atm for 15 min. The growth conditions are optimized to achieve large-areas
 110 of ML and BL graphene. The C-face 4H-SiC(000 $\bar{1}$) surface was chemical-mechanical polished (epi-ready surface). The substrate was cleaned using the standard Radio Corporation of America cleaning procedure, followed by dipping it into HF solution to remove the C-face SiC surface native oxide.

The number of graphene layers and their distribution across the sample

115 were determined using reflectance mapping and line-scans [29]. The method
 makes use of the fact that the reflectance of graphene on SiC normalized to
 the reflectivity of bare substrate increases linearly with 1.7% per layer for
 up to 12 layers [29]. For the line-scans the reflectance was measured along
 lines with 2 mm length and a step of 1 μm . Reflectance mapping over areas
 120 of $30\times 30\mu\text{m}^2$ with a step size of 0.3 μm was performed on several differ-
 ent locations of the sample. In addition, μ -Raman scattering (μ -RS) maps
 over areas with sizes of $10.5\times 10.5\mu\text{m}^2$ and a step of 0.3 μm were simulta-
 neously recorded with corresponding reflectance maps with the same sizes.
 This allowed to assign a specific μ RS spectrum to the respective number
 125 of layers and draw a conclusion about the properties of graphene, such as
 coupling/decoupling, doping, and strain in relation to the number of layers.
 A diode-pumped semiconductor laser with a wavelength of 532 nm (photon
 energy $E_L=2.33\text{ eV}$) was used as an excitation source for the reflectance and
 μ RS measurements. The laser spot diameter was $\sim 850\text{ nm}$ using a $100\times$
 130 objective. The μ RS spectra of C-face graphene are obtained by subtracting
 a reference Raman spectrum of 4H-SiC(000 $\bar{1}$) from the measured spectra.

The surface morphology and the local work function were investigated
 using scanning Kelvin probe microscopy (SKPM). The SKPM measurements
 were performed at room temperature and ambient conditions using a Veeco
 135 DI 3100 scanning probe microscope equipped with Nanoscope *IV* controller.

Complementary electrical information is obtained by torsion resonance
 conductive atomic force microscopy (TR-CAFM) that was used to measure
 simultaneously topographic and current maps. TR-CAFM is a dynamic scan-
 ning probe method which allows non destructive electrical measurements

140 from a conductive tip oscillating in a torsional or twisting mode in close
 proximity to the sample surface (0.33 nm). This non contact method has a
 distinct advantage over the conventional conductive atomic force microscopy
 (CAFM) performed in contact mode because of the absence of shear forces
 that can be damaging for the graphene sheets [30]. Measurements were
 145 carried out using a Veeco DI3100 AFM with Nanoscope V controller and
 tunneling atomic force microscopy (TUNA) application module. Platinum-
 coated Si tips with a typical apex radius of 10-20 nm were used. During
 a surface scan, a DC bias is applied between the tip and the sample back-
 side and nanoscale resolution maps of the tunneling current flowing vertically
 150 through the graphene/SiC interface were collected. From a selected position
 of the current maps, a local $I-V_{tip}$ measurements were carried out by scan-
 ning current spectroscopy where the conductive tip is in direct contact with
 graphene. The local $I-V_{tip}$ measurements provide direct information on the
 electrical properties of the graphene/SiC interface. It is worth noting that
 155 the contact between the metal tip and graphene is Ohmic, with a contact
 resistance that can be reduced down to few kohms by properly setting the
 tip/sample force. Furthermore, as will be evident from the experimental
 $I-V_{tip}$ characteristics, the semi-insulating SiC substrate introduces a series
 resistance contribution limiting the current flowing through graphene/SiC
 160 Schottky contact at higher bias values

The structural properties of graphene and their temporal evolution were
 studied by low energy electron microscopy (LEEM), low energy electron
 diffraction (micro-LEED), X-ray photoelectron emission microscopy (XPEEM)
 and X-ray photoelectron microspectroscopy (micro-XPS). The measurements

165 were performed on the same sample over a period of two years using the
ELMITEC-LEEM III instrument at the I311 beamline of the MAX-Lab syn-
chrotron radiation facility in Lund, Sweden. We note that multiple sample
locations (center, periphery and in-between) were probed, and in which of
those several (at least five) areas with a given number of graphene layers
170 were measured.

Landau level spectroscopy was performed using an optical Hall effect
(OHE) instrument [31] in the mid-infrared spectral range from 550 cm^{-1} to
 4000 cm^{-1} with a resolution of 1 cm^{-1} , at a temperature of 1.5 K and at
an angle of incidence of 45° . The probing area of the OHE measurements
175 covered the whole sample of $15\times 15\text{ mm}^2$. The magnetic field component
with a direction perpendicular to the sample was varied from 0 to 5.66 T.
The measurements were performed using generalized ellipsometry and the
Mueller matrix formalism was used to report the OHE data [31]. The OHE
data are presented as differences between measurements at a certain magnetic
180 field and zero field.

3. Results and discussion

3.1. Thickness distribution and ordering of FLG

Based on a large number of thickness maps and line-scans obtained from
reflectance, and LEEM images taken at different locations of the sample it
185 is determined that the C-face graphene consists predominantly of ML and
BL graphene. Typical distributions of the number of graphene layers are
exemplified in Figs. 1a and b, showing representative thickness line-scan and
a map, respectively. The analysis of the number of graphene layers from

the line-scan renders 45% ML, 18% BL graphene, 3% bare substrate where
 190 graphene did not form, and the remaining part is FLG (≥ 3 ML). These results
 are further confirmed by the **thickness mapping obtained from reflectance**
 (Fig. 1b) and LEEM imaging (Figs. 2a-c). The ML and BL domains form
 predominantly as stripes (Figs. 1b, 2a and 2b) following the SiC terraces and
 in large domains with constant thickness, e.g., with size as large as $\approx 500 \mu\text{m}^2$
 195 for the ML graphene in Fig. 2a. This is in contrast with previous reports
 on islanding of graphene with relatively small domain size when grown in
 Ar atmosphere [32, 33, 20]. A possible reason for these differences may be
 the fact that our graphene is grown at much higher temperature (1950 $^{\circ}\text{C}$)
 compared to conventional graphene grown in Ar atmosphere (below 1550
 200 $^{\circ}\text{C}$) [32, 33, 20]. The higher growth temperature enables enhanced carbon
 diffusion and surface restructuring. We also note that the domain size with
 uniform thickness in our case is larger than previously reported for high-
 temperature sublimation C-face graphene [22, 23].

Figure 1: (a) Distribution of the number of graphene layers determined from a reflectance line scan of 2 mm length and (b) $30 \times 30 \mu\text{m}^2$ thickness map obtained from the corresponding reflectance map. (A color version of this figure can be viewed online.)

Representative LEEM images taken from different areas of the sample
 are shown in Figs. 2a-c. Domains with different contrasts corresponding
 to a different number of graphene layers, as indicated in the images, are
 clearly visible. The determination of the number of graphene layers was made
 combining LEEM, LEEM- $I(V)$ curves, μ -LEED and XPEEM. Examples of
 ML, BL and TL graphene domains are indicated in Figs. 2(a)-(c). In most
 of the areas large domains with homogeneous ML and BL graphene have
 formed (Figs. 2a and b) in agreement with the **thickness mapping results
 obtained from reflectance**. Few areas where the domain sizes with uniform
 thickness are significantly smaller (Fig. 2c) can also be found. In the latter,
 the graphene patches appear as mixtures of ML+BL or BL+TL graphene.
 Respective LEEM- $I(V)$ curves taken from the homogeneous ML, BL and
 TL domains, indicated in Figs. 2(a)-(c) with circles, are shown in Fig. 2(d).
 It can be seen that in addition to the one and two minima observed in the
 LEEM- $I(V)$ curves of ML and BL graphene, respectively, an extra peak is
 detected in both cases and attributed to the presence of an interface layer
 (indicated by arrows). In order to gain further insight into the interface and
 structural properties of ML, BL and TL graphene domains, μ -LEED and
 XPEEM are performed in the respective regions. The μ -LEED diffraction
 patterns taken at two different electron energies each from the homogeneous
 ML, BL and TL graphene domains indicated by circles in Fig. 2(a)-(c) are
 shown in Fig. 3.

The μ -LEED patterns collected from the ML domain using an electron
 energy of 42 eV shows single 1×1 diffraction pattern of graphene (indicated
 by $\vec{g}_1$ and $\vec{g}_2$ in Fig. 3(a)) with unique azimuth orientation. The diffuse clouds

Figure 2: LEEM images taken at different locations of the sample and recorded with electron energy and a field of view of: (a) 1.5 eV and 50 μm , respectively; (b) 1.5 eV and 50 μm , respectively and (c) 5.6 eV and 15 μm , respectively. Exemplary homogeneous ML, BL and TL graphene domains, as well as areas with mixed number of graphene, ML+BL and BL+TL, are indicated. (d) LEEM-I(V) curves taken from the homogeneous ML, BL and TL domains indicated with circles in (a), (b) and (c), respectively. (A color version of this figure can be viewed online.)

seen around the graphene diffraction spots can be caused by corrugation of the graphene layer or by a presence of an inhomogeneous interface layer. At higher electron energy of 74 eV (Fig. 3(d)) the six-fold SiC 1×1 diffraction spots (indicated by $\vec{S}_1$ and $\vec{S}_2$) become visible. The relative orientation of the graphene and SiC diffraction patterns shows that the single domain ML graphene is rotated by $\sim 12^\circ$ with respect to the substrate. Previously, C-face ML graphene was reported to be rotated by 30° with respect to SiC [5]. Multiple or single domains of C-face graphene rotated by $\pm 1^\circ$, $\pm 7^\circ$, $\pm 10^\circ$ and 30° with respect to SiC 1×1 , have also been reported for adjacent layers within FLG. We note that a single graphene domain with unique azimuth orientation is observed in all ML regions in our sample. However, in some of these regions we could not resolve the SiC diffraction spots at higher electron energies, which might be related to a thicker interface layer. A similar effect is also observed in the BL regions of the sample - no diffraction patterns from SiC could be seen even at an electron energy of 80 eV (Fig. 3(e)).

Figure 3: μ -LEED diffraction patterns collected from the homogeneous regions indicated in Fig.2(a) - (c) with circles: (a), (d) ML graphene area with a diameter of $4.5 \mu\text{m}$ (indicated by a circle in Fig. 2a) and electron energies of (a) 42 eV and (d) 78 eV; (b), (e) BL graphene area with a diameter of $4.5 \mu\text{m}$ (indicated by a circle in Fig. 2b) and electron energies of (b) 45 eV and (e) 80 eV; and (c), (f) TL graphene area with a diameter of $1\mu\text{m}$ (indicated by a circle in Fig. 2c) and electron energies of (c) 45 eV and (f) 80 eV. The reciprocal lattice vectors of graphene ($\vec{g}_1$ and $\vec{g}_2$) and SiC ($\vec{S}_1$ and $\vec{S}_2$) are indicated in the figures. The circles in (c) and (f) highlight the superstructure diffraction spots. (A color version of this figure can be viewed online.)

The μ -LEED diffraction pattern of BL graphene taken at 42 eV (Fig. 3(b)) shows six graphene diffraction spots ($\vec{g}_1$ and $\vec{g}_2$) similar to the case of ML graphene. Note that the single diffraction patterns observed in Figs. 3(b) and (e) indicate that there is no rotational disorder between the adjacent graphene layers in the BL graphene stack.

The μ -LEED diffraction pattern of TL graphene collected using an electron energy of 45 eV shows graphene 1×1 diffraction pattern similar to

ML and BL graphene, and a superstructure (indicated by circles) around the spots of the 0-order and 1×1 graphene diffraction pattern (Fig. 3(c)). Similar superstructure spots were previously observed for C-face TL graphene and suggested to be due to an interface layer akin to the buffer layer present in the case of Si-face graphene [22]. However, in Ref. [22] the energy dependence of the diffraction pattern was not investigated to confirm this suggestion. When the electron energy is increased up to 80 eV, the superstructure diffraction spots around the 0-order disappear and the intensity of the superstructure diffraction pattern located around the 1×1 spots for our TL graphene is considerably reduced (Fig. 3(f)). These results suggest that the observed superstructure spots are unlikely to originate from the SiC reconstruction or from an interface layer, but may be rather a result of double scattering. Another possible origin of the extra spots could in principle be an out-of-plane rotation between the second or first layers with respect the top graphene layer. If this was the case, increasing electron energy would at least keep the spot intensity ratio the same or even make the contribution from the second/first layer stronger (i.e. the intensities of the extra spots would increase). In contrast, one can see a significant decrease of the extra spots intensities when the probing energy increases from 45 to 80 eV (see Figs. 3(c) and S.1(c) supplementary material). Consequently, out-of-plane rational disorder can be also ruled out for TL graphene. We note that the superstructure spots were never observed for BL graphene but could be found in the case of TL graphene grown on C-face 3C-SiC [34].

3.2. Interface layer properties

Figure 4(a) shows a C 1s XPEEM image taken at photon energy of 330 eV from the same region shown in Fig.2b. Representative μ -XPS C 1s and Si 2p core-level spectra taken from the homogeneous ML and BL graphene are shown in Figs. 4 (b) and (c), respectively. The C 1s and Si 2p spectra are measured with photon energy of 332 eV and 200 eV, respectively. The C

Figure 4: (a) C 1s XPEEM image with a field of view of $50 \mu\text{m}$ taken at photon energy of 330 eV with an electron energy of 41 eV; μ -XPS spectra of regions with different thickness: (b) C 1s peak measured using a photon energy 332 eV for homogeneous ML and BL graphene; (c) Si 2p peak measured at 200 eV for homogeneous ML and BL graphene. (A color version of this figure can be viewed online.)

1s core-level spectra of ML and BL graphene show the characteristic single narrow peaks associated with the $\text{C}^{sp2}\text{-C}^{sp2}$ bonds typical for C-face graphene [16]. The $\text{C}^{sp2}\text{-C}^{sp2}$ peaks are located at 284.48 eV and 284.6 eV for ML and BL graphene, respectively. This result indicates that the work function of ML graphene is higher than for BL graphene, which can be related to different doping levels or/and different band structures of ML and BL graphene. Two well resolved peaks can be seen in the Si 2p core-level spectra of ML and BL graphene (Fig. 4(c)). The first peak located at 100.8 eV originates from the SiC substrate. The second peak at 102.9 eV can be associated with

silicon to oxygen bonds, which we attribute to the presence of an interface
 290 SiO_x layer. The latter provides a possible explanation for the clouds **ob-**
served in the graphene μ -LEED diffraction pattern (Fig. 2(a)). The oxide
 peak is wide suggesting a broad distribution of oxidation states. No amor-
 phous carbon could be identified at the interface between graphene and the
 substrate, as previously reported for C-face graphene grown by confinement
 295 controlled sublimation [20, 21] or on mechanically polished 4H-SiC(000 $\bar{1}$) by
 high temperature sublimation [23, 24].

In order, to investigate the effect of aging on the interface properties of
 graphene, Si 2P μ -XPS spectra of ML graphene are measured after storing
 the sample for 24 months at room temperature in ambient conditions. The
 300 measurements were performed in a number of sample locations and similar
 results were obtained in all cases. Representative Si 2P μ -XPS spectra of
 as-grown ML graphene and ML graphene after 24 months of aging are shown
 in Fig. 5. It is clearly seen that the ratio between the SiO_x and the SiC peak
 intensities $[I(\text{SiO}_x)/I(\text{SiC})]$ increases with time. This is accompanied with a
 305 slight decrease of the peak separation suggesting that **after 24 months the**
oxide composition is approaching SiO_2 for ML graphene. The results indi-
 cate that the SiO_x interface is changing with time, its chemical composition
 gets closer to SiO_2 and its thickness increases **with aging at normal ambi-**
ent conditions. The latter is further supported by reflectance measurements
 310 performed on the sample over a period of two years.

Fig. 6 shows the reflectance of the as-grown (a) and after 24 months of
 aging graphene (b) together with the bare 4H-SiC substrate reference. The
 reflectance of as-grown ML graphene is 1.8% higher than the average re-

Figure 5: Representative Si 2p μ -XPS spectra using a photon energy of 200 eV of as-grown ML graphene (dots) and ML graphene after 24 months of sample storing under normal ambient conditions (line). (A color version of this figure can be viewed online.)

flectance of the bare 4H-SiC(000 $\bar{1}$) substrate in agreement with Ref. [29]. In
 315 contrast, the reflectance of ML graphene after 24 months of aging (Fig. 5(b))
 is only 0.47% higher than the reference reflectance of bare 4H-SiC. Note that
 the difference in reflectance of two consecutive graphene layers, e.g., ML/BL
 and BL/TL, is always the same - 1.7%. The observed differences in the re-
 flectance of ML graphene with respect to the substrate for as-grown graphene
 320 and after aging can be understood considering the presence of interface SiO_x
 layer. It is well known that native SiO₂ may act as anti-reflective coating
 for a particular thickness. Therefore, the observed low reflectance of ML
 graphene after 24 months can be explained by an increased thickness of the
 SiO_x interface layer in agreement with the μ -XPS results (Fig. 5).

325 We suggest that the observed SiO_x at the interface between graphene and

Figure 6: Reflectance of graphene (black dots) and a bare 4H-SiC substrate reference (red triangles): (a) as-grown and (b) after 24 months of aging. (A color version of this figure can be viewed online).

SiC is formed by oxidation of Si atoms trapped at the interface, which can be related to the specifics of the sublimation process. During the sublimation process, Si atoms are transported from the bulk of SiC to its surface followed by their desorption. As a result, a C-rich environment at the surface is created and which enables the graphene growth. The growth of subsequent graphene layers depends on the capability of the Si atoms to diffuse and desorb. After the formation of graphene, the desorption of Si atoms becomes difficult, which can lead to an excess of Si atoms trapped at the interface. Then Si oxidation might occur after graphene growth due to the presence of oxygen in the environment and as a result of exposure to normal ambient [35, 36]. This is consistent with the observed time evolution of the interface layer thickness. We believe that oxidation of SiC during growth is unlikely since SiO_x was reported to be stable up to a temperature of 1600 °C [26] while our growth temperature is 1950°C. Our ML graphene shows a relatively high density of defects, which may facilitate the oxygen diffusion and oxidation of

Si (See section 3.4: Doping and defects).

3.3. Surface potential, conductivity mapping, and transport of FLG

Kelvin probe measurements over areas of few mm gives an average graphene work function W_G of about 5.00 eV, which is higher than the work function of undoped graphene ($W_{GN} = 4.5$ eV) [37]. This indicates that the average doping of our graphene sample is p -type, which is also confirmed by terahertz OHE (not shown here). Local SKPM measurements show that ML graphene has a higher p -type doping compared to FLG (See section S.2 in the supplementary material). We use TR-CAFM to get insight in the mechanisms of current transport across the graphene/SiC(000 $\bar{1}$) interface. A representative AFM morphology and the corresponding current map both acquired in the torsion resonance mode are presented in Fig. 7(a) and (b), respectively. FLG areas (BL, TL and multilayers) can be identified by the presence of higher wrinkles than in the ML regions. Interestingly, from the current map in Fig. 7(b), a significantly lower current level can be observed in the ML graphene regions with respect to FLG. To investigate these electrical conduction differences through ML and FLG interfaces with SiC(000 $\bar{1}$), local current-voltage characteristics (I - V_{tip} , with V_{tip} the tip bias) have been performed at several positions on the scanned area. Two representative I - V_{tip} characteristics measured on the ML and FLG regions are shown in Fig. 7(c). A clear rectifying behavior is observed for the ML graphene contact to SiC(000 $\bar{1}$), while symmetric I - V_{tip} characteristics are measured on the FLG regions. These striking differences in the vertical conduction can be ascribed, in a simple approximation, to the higher work function value of ML areas with respect to FLG detected by SKPM.

Figure 7: (a) TR-CAFM topography and (b) the corresponding current map of C-face graphene with ML and FLG regions indicated. (c) Representative I - V_{tip} characteristics measured on the ML and FLG regions. (d) Semilog-scale plot of the local I - V_{tip} characteristic measured on ML graphene and fitting of the linear region with the thermionic emission law (the obtained Schottky barrier height $\phi_B = 0.73$ eV and ideality factor $n = 7.8$ are indicated). (e) Schematic band diagram of the ML/SiC(0001) contact with a SiO_x interface layer with a thickness δ which accounts for the difference $\Delta = 1.2$ eV between the experimental and ideal SBH values. (A color version of this figure can be viewed online.)

In general, for an ideal graphene/SiC Schottky contact (no interface layer exists between graphene and SiC), the Schottky barrier height (SBH) is expected to increase with graphene work function resulting in a reduced thermionic emission current above the barrier. However, in our graphene sample a substoichiometric SiO_x layer between graphene and SiC is present as inferred by μ -LEED, μ -XPS and reflectance analyses. The presence of such an interface layer is expected to play a key role in the graphene/SiC contact properties causing a deviation from the ideal Schottky-Mott behav-

ior. To extract more quantitative information on the contact properties, the local I - V_{tip} characteristic measured on the ML graphene region is reported in Fig. 7(d) on a semilog-scale and the fitting of the linear region with the thermionic emission law is carried out. The obtained values of the SBH and ideality factor are $\phi_B = 0.73$ eV and $n = 7.8$, respectively. The experimental n value is much higher than unity and clearly indicates that the ML/SiC(000 $\bar{1}$) contact cannot be described as an ideal Schottky contact. Furthermore, the obtained SBH value for graphene on SiC(000 $\bar{1}$) is much lower than the ideal one expected according to the Schottky-Mott relation $\phi_B = W_G - \chi = 1.9$ eV, being $W_G = 5$ eV the average graphene work function measured by Kelvin probe measurements and $\chi = 3.1$ eV the 4H-SiC electron affinity. These deviations from the ideal behavior can be described according to the Card-Rhoderic model for metal/semiconductor junctions with an interfacial layer [38], considering the effect of the SiO_x layer with thickness δ , which introduces a density of interface states D_{it} between graphene and SiC. Fig. 7(e) shows a schematic band diagram of the ML graphene/SiC contact with this thin insulating layer, which accounts for the difference $\Delta = 1.2$ eV between the experimental and ideal SBH values. Furthermore, the strong deviation of the ideality factor from unity can be explained in terms of a high interface-states density D_{it} , according to the relation [38]:

$$n = 1 + \frac{e\delta D_{it}}{\epsilon_i \epsilon_0} \quad , \quad (1)$$

where ϵ_i and ϵ_0 are SiO_x dielectric constant and the vacuum permittivity, respectively. Assuming a dielectric constant of 3.9 [39] for the SiO_2 interface layer, we estimate a linear density of interface defects $\delta D_{it} = 1.47 \times 10^7$

$\text{cm}^{-1}\text{V}^{-1}$.

3.4. Doping and defects of FLG

More detailed information on doping of FLG can be obtained from the μRS analysis. Figs. 8(a) and (b) show representative μRS spectra taken from ML and BL graphene regions, where the D, G, D' and 2D peaks associated with graphene can be resolved [35]. In addition, a peak in the vicinity of the G peak is also detected in the μRS spectra of ML graphene. This peak, hereafter referred to as the B peak, is located around 1590 cm^{-1} on the low-energy side of the G peak (see Fig. 8b). In BL graphene no B peak can be resolved. Therefore, the Raman spectra in the vicinity of the G peak are fitted with three Lorentzian lineshapes accounting for the B, G and D' peaks in ML graphene, and using two Lorentzian lineshapes accounting for the G and D' peaks in the case of BL graphene, respectively. The D and the 2D peaks are fitted each with a single Lorentzian lineshape for all graphene layers. (See Fig.S3 for the full width at half maximum (FWHM), of G and 2D peaks, and the B peak intensity in supplementary material)

It is seen from Fig. 8 that the G-, ω_G , and the 2D-, ω_{2D} , peak positions for both ML and BL graphene are blue-shifted with respect to the corresponding positions for freestanding graphene [40] with $\omega_{G,0} = 1582\text{ cm}^{-1}$ and $\omega_{2D,0} = 2670\text{ cm}^{-1}$. The observed shifts might be due to a compressive biaxial strain and/or doping. The biaxial strain results from a difference in thermal expansion coefficients of graphene and SiC. The doping is due to a charge transfer from the SiC substrate and/or impurity incorporation [41, 42]. The

Figure 8: (a) Representative μ RS spectra of ML (black solid line) and BL (red dashed line) graphene. The dotted lines indicate the G and 2D peaks positions of freestanding graphene ($\omega_{G,0} = 1582 \text{ cm}^{-1}$ and $\omega_{2D,0} = 2670 \text{ cm}^{-1}$). (b) Enlarged Raman spectra from (a) in the vicinity of the G peak. (A color version of this figure can be viewed online.)

G (2D) peak position shift due to biaxial strain (ε) is described by:

$$\Delta\omega_{G(2D)}^b = -2\omega_{G(2D),0}\gamma_{G(2D)}\varepsilon \quad , \quad (2)$$

where $\gamma_{G(2D)}$ is the Grüneisen parameter of the G(2D) peak. We use $\gamma_G = 1.8$ and $\gamma_{2D} = 2.7$ [43, 44] resulting in a $(\Delta\omega_{2D}/\Delta\omega_G)^b$ ratio of 2.53 as shown by a line in Fig. 9, referred hereafter as the biaxial strain line.

Figure. 9 shows a plot of the 2D versus G peak positions for ML (dots) and BL (triangles) graphene. The shifts of G and 2D peak positions for ML graphene with respect to the biaxial strain line indicates that ML graphene is highly doped. These results are in agreement with the SKPM observations (see section S.2 in supplementary material). On the other hand, the G and 2D peak positions for BL graphene are very close to the biaxial strain line implying very low doping levels in this case. The former is further confirmed by comparing the ratio between 2D and G peak intensities, $I(2D)/I(G)$. BL

graphene shows a higher 2D peak intensities compared to the G peak, which is a signature of low doped graphene [45]. In contrast, ML graphene has much lower $I(2D)/I(G)$ ratios indicating a higher free charge carrier concentration (see Fig. 8) [45].

Figure 9: Experimental 2D peak position, (ω_{2D}) , versus G peak position, (ω_G) , for ML (dots) and BL (triangles) graphene. The blue solid line represents the shifts due to biaxial compressive strain according the theoretical ratio $((\Delta\omega_{2D}/\Delta\omega_G)^b = 2.53)$. The G and 2D positions of freestanding graphene (ω_{G0} and ω_{2D0}) are indicated by an asterisk. The histograms of the G peak and 2D peak positions for ML and BL graphene are shown in the insets. The color bar represents the 2D peak FWHM. (A color version of this figure can be viewed online.)

The free hole concentration in ML graphene is estimated from the experimental shifts of the G and 2D peaks with respect to free-standing graphene $\Delta\omega_{G(2D)}$ assuming that they are linear combination of the respective shifts due to biaxial strain, $\Delta\omega_{G(2D)}^b$, and doping, $\Delta\omega_{G(2D)}^h$ [46]:

$$\Delta\omega_{G(2D)} = \Delta\omega_{G(2D)}^h + \Delta\omega_{G(2D)}^b, \quad (3)$$

400 Equation 3 is solved taking into account Eq.2 and assuming $\gamma_G = 1.8$ and $\gamma_{2D} = 2.7$ [43, 44], $\delta\omega_G^h/\delta E_F = 42 \text{ cm}^{-1} \text{ eV}^{-1}$ and $\delta\omega_{2D}^h/\delta E_F = 32 \text{ cm}^{-1} \text{ eV}^{-1}$

reported for gated pristine graphene [45]. The average Fermi energy for ML graphene is 0.480 eV and the respective average free hole concentration is $1.4 \times 10^{13} \text{cm}^{-2}$ (See Fig.S3(e) in the supplementary material for the free hole density map of ML graphene).

The free hole concentration can be anti-correlated with the B peak intensity - the lower the free hole concentration the higher the B peak intensity (see Fig. S3(d) and (e) in the supplementary data). The B peak observed in the Raman spectra of ML graphene at 1590 cm^{-1} has not been reported before. We speculate that the B peak might be due to the presence of small BL domains in the ML graphene regions. This is based on the XPEEM results showing ML graphene regions containing inclusions of BL graphene and considering the lower doping of BL compared to ML graphene. Furthermore, the B peak position seems to be very close to the G peak position of BL graphene (see Fig. S3(b) in the supplementary data). Such BL inclusions could be expected to generate defects in the ML regions where they occur. Indeed, a correlation between the B peak intensity and defect density is observed (See Fig. S3(f) in the supplementary material). A defect density of the order of 10^{11}cm^{-2} is estimated for ML and BL graphene (See Fig.S3(f) in the supplementary material for the defect density map of ML graphene), which is in line with our speculation that defects may be a potential path for oxygen diffusion after growth causing the formation of the observed SiO_x interface layer. Dislocations, disclinations and boundary defects generated at the grain boundaries [47], as a result of the three-dimensional growth of C-face graphene, are potential candidates to explain the origin of the large defect density in ML and BL graphene observed here.

3.5. Decoupling of individual layers in FLG

Analysis of the Raman 2D peak shape also allows to draw conclusion about the coupling of the adjacent layers in FLG. In general, the 2D peak
430 shape and FWHM depend on the number of graphene layers and their coupling following the change of electronic band structure [48]. For example, exfoliated ML graphene on SiO₂/Si shows a symmetric 2D peak with Lorentzian shape and a FWHM $\simeq 24 \text{ cm}^{-1}$, while coupled AB-stacked BL graphene shows a broader and asymmetric 2D peak with a FWHM $\simeq 55 \text{ cm}^{-1}$, and
435 can be fitted with four Lorentzian lineshapes [48]. C-face graphene typically consists of decoupled graphene layers, i.e., the graphene stack exhibits the same electronic band structure as that of a ML graphene. Hence, the 2D peak of decoupled FLG, similarly of the 2D peak of ML graphene, can be fitted with a single Lorentzian lineshape with FWHM in the range 24 -
440 40 cm^{-1} [49]. The 2D peak of our ML and BL graphene has a symmetric Lorentzian lineshape with average FWHM of 39 cm^{-1} and 31 cm^{-1} for ML and BL, respectively (see Fig. S3(c) in the supplementary data). This result indicates that the graphene layers in the BL stack are decoupled. The somewhat broader 2D peak of ML graphene compared to BL graphene may
445 be explained by the higher hole doping of the former as inferred by μ RS and SKPM. An increase of the 2D FWHM with increasing doping concentration was previously reported and attributed to free charge carrier interactions [50, 51]. We note that TL graphene also shows a 2D peak with an average FWHM below 40 cm^{-1} indicating that the graphene layers in the TL
450 graphene stack are also decoupled.

Further insight into the interaction between the adjacent graphene lay-

Figure 10: (a) On-diagonal block $\delta M_{33}/M_{11}$ optical Hall effect spectra for different values of the magnetic field. The spectra are measured at 1.5 K and shifted by 0.01 for clarity. (b) LL transition energy positions as a function of magnetic field. The blue dashed and red solid lines represent calculated transition energies for single layer graphene with Fermi velocities of $\tilde{c}_1 = 1.03 \times 10^6 \text{ m.s}^{-1}$ and $\tilde{c}_2 = 1.09 \times 10^6 \text{ m.s}^{-1}$, respectively. (A color version of this figure can be viewed online.)

ers in the graphene stack can be gained from inter-Landau-level (LL) spectroscopy. It is well established that ML graphene and stacks of decoupled graphene layers show a characteristic square-root dependence of the LL transition energies on magnetic field [52]. On the other hand, coupled AB BL, TL etc. graphene show sublinear dependence of the LL transitions on magnetic field [53]. We have recently shown that LL transitions can be measured by mid-infrared optical Hall effect (OHE) in oblique-incidence reflection mode and that single layer graphene or a stack of decoupled graphene layers exhibit transitions with polarization preserving selection rules while those for coupled graphene layers have polarization-mixing character [54]. In our graphene sample we observe LL transitions only in the block-on diagonal Mueller matrix element spectra indicating polarization preserving selection rules of the transitions and thus decoupled graphene layers in the FLG stack [54]. Fig. 10 (a) shows exemplary OHE difference spectra for one

of the block on-diagonal Mueller matrix elements, $\delta M_{33}/M_{11}$, and for different magnitudes of the magnetic field. The LL transitions are indicated with letters following the notations of Sadowski *et al.* [52]. Note that LL transitions from ML graphene in our case cannot be detected due to the high free hole concentration. As a result of the high *p*-type doping of ML graphene ($E_F=0.480$ eV) even for the highest magnetic field of 5.66 T used in our MIR OHE experiments, the LL transitions from ML graphene occur outside the measured spectral range. Therefore, all measured LL transitions in our sample must originate from BL, TL and FL graphene, which show a lower doping as deduced from μ RS and SKPM (Figs. 9 and section S.2 in the supplementary material). The double peak structure of the LL transitions in Fig. 10 (a) can be associated with the presence of vacancy defects [55].

The energy positions of the LL transitions determined from the OHE data are plotted as a function of the magnetic field in Fig. 10 (b). A square root dependence with the magnetic field, characteristic for a single graphene layer [52] is observed. This result implies that the adjacent layers in our BL, TL, and FLG are decoupled and behave as a stack of non-interacting graphene layers. In such a case, the LL transition energies, E_n , can be described by $E_n = \text{sgn}(n)\tilde{c}\sqrt{2e\hbar B|n|}$ where $\tilde{c}$ is the average velocity of the Dirac fermions. We obtain from the fit of the data in Fig. 10 (b) Fermi velocities of $\tilde{c}_1 = 1.03 \pm 0.01 \times 10^6$ m s⁻¹ and $\tilde{c}_2 = 1.09 \pm 0.01 \times 10^6$ m s⁻¹. These values are in good agreement with previously published results for decoupled C-face graphene [52, 54, 55].

The facts that we only observe LL transition energies with polarization preserving selection rules and a square-root dependence on the magnetic

field, as well as the symmetric shape of the Raman 2D peak with an average FWHM below 40 cm^{-1} indicate that adjacent layers in our BL, TL and FLG stacks are decoupled. Such behavior was previously observed for C-face graphene and attributed to rotational disorder of the adjacent graphene layers in the stack [18, 21]. However, the μ -LEED patterns taken from different BL and TL regions of our sample show single 1×1 diffraction pattern of graphene (Fig. 3) with no out-o-plane rotation. Thus, our results indicate that BL, TL, and FL graphene are composed of decoupled graphene layers but are not rotationally disordered. The origin of layer decoupling in this case needs to be further investigated. A possible explanation is trapping of impurity atoms, such as Si or O between the layers in the stack, which may cause an increase of layer spacing and their electronic decoupling.

Our results on the decoupling of C-face FLG grown by high-temperature sublimation are in contrast with a recent report on AB stacked C-face graphene grown at 1900°C [25]. Note that the decoupling in our case is inferred based on MIR OHE measurements that are probing the whole area of the sample and based on a large sampling of μ RS maps across the sample. In contrast, the AB stacking order in [25] is inferred based on nano-ARPES measurements probing limiting area of the FLG. It is well known that C-face graphene consists of domains with multi-layers with varying thicknesses as also evidenced in this work [26, 27, 22, 20]. Furthermore, substrate defects may cause the formation of graphitic AB stacked inclusions within decoupled graphene stacks [54]. For example, we have previously shown that when grown on SiC substrate with polishing defects C-face graphene is predominantly AB stacked [23]. AB stacking was also previously evidenced in the

Raman spectra of C-face graphene nucleated at dislocations [56]. Therefore, nanoscale characterization techniques, which provide local information, may be best augmented with macroscopic techniques to draw comprehensive conclusions about the nature of C-face graphene, which is typically highly
520 inhomogeneous

4. Summary

The interface structure and its implications for electrical transport, stacking order and decoupling of FLG on C-face 4H-SiC (0001) are investigated using multi-scale advanced characterization tools. Graphene is grown by
525 high-temperature sublimation in argon atmosphere at optimal conditions to achieve large-area domains (few hundreds of μm^2) with uniform ML, BL and TL graphene. However, fewer regions where graphene grows as mixtures of ML+BL and BL+TL with significantly smaller domain sizes, as well as thicker regions with ≥ 3 MLs could also be found. Single 1×1 diffraction
530 pattern is revealed by μ -LEED for ML, BL and TL graphene. We find that the large-area uniform ML graphene is a single crystallographic grain with unique azimuth rotation rotated by $\approx 12^\circ$ with respect to SiC. Furthermore, BL and TL graphene do not show out-of-plane rotational disorder of the adjacent layers in the stack, which is in agreement with previous results for
535 high-temperature C-face graphene [22].

An interface SiO_x layer is identified between C-face graphene and SiC independently of graphene thickness and domain size. We suggest that the SiO_x layer forms after growth as a result of oxidation of trapped Si atoms during the sublimation process, and speculate that defects in ML and BL

540 graphene serve as diffusion paths for oxygen. We find that the chemical composition of the interface layer changes towards SiO_2 and its thickness increases with aging in normal ambient conditions. TR-CAFM investigations show that the presence of the interface layer causes the formation of non-ideal Schottky contact between ML graphene and SiC, which is associated with a
545 large density of interface defects.

A correlation between SKPM and μRS shows that ML graphene is highly p -type doped with an average hole density of $1.4 \times 10^{13} \text{cm}^{-2}$ while BL and FL graphene have much lower free-charge carrier concentration below 10^{12}cm^{-2} . These results are consistent with vertical current transport measurements
550 across graphene/SiC interface by TR-CAFM mapping and local current-voltage analyses.

Mid-infrared optical Hall effect measurements revealed Landau-level transitions in FLG that have a square-root dependence on magnetic field, which is characteristic for single layer graphene. This allows us to conclude that
555 FLG consists of decoupled layers, which is further confirmed by μRS analysis. Contrary to previous works on decoupled C-face graphene, our $\mu\text{-LEED}$ investigations indicate that the adjacent layers in the BL and FLG stack are not rotationally disordered. Our results imply that the nature of C-face graphene is rather complicated and depends on growth conditions, substrate preparation, temperature, etc., in contrast to epitaxial graphene on Si-face
560 SiC(0001) that shows coupled graphene layers with AB stacking, rather independent of growth conditions. Our findings on the interface layer and its implications for the electrical properties of FLG suggest that C-face ML and BL graphene grown by high-temperature sublimation are not optimal for de-

565 vice fabrication. On the other hand, thicker C-face graphene with decoupled adjacent layers have better perspective for future electronic applications.

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