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Exploring graphene formation on the C-terminated face of SiC by structural, chemical and electrical methods

Cristina E. Giusca,^{1,} Steve J. Spencer,¹ Alex G. Shard,¹ Rositza Yakimova,² and Olga Kazakova¹*

¹ National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, United Kingdom

² Department of Physics, Chemistry and Biology, Linköping University, S-58183 Linköping, Sweden

Abstract

The properties of epitaxial graphene on the C-face of SiC are investigated using comprehensive structural, chemical and electrical analyses. By matching similar nanoscale features on the surface potential and Raman spectroscopy maps, individual domains have been assigned to graphene patches of 1-5 monolayers thick, as well as bare SiC substrate. Furthermore, these studies revealed that the growth proceeds in an island-like fashion, consistent with the Volmer-Weber growth mode, illustrating also the presence of nucleation sites for graphene domain growth. Raman spectroscopy data shows evidence of large area crystallites (up to 620 nm) and high quality graphene on the C-face of SiC. A comprehensive chemical analysis of the sample has been provided by X-ray photoelectron spectroscopy investigations, further supporting surface potential mapping observations on the thickness of graphene layers. It is shown that for

* Corresponding author: Tel.: +44 (0) 20 8943 6123. E-mail: cristina.giusca@npl.co.uk (Cristina Giusca)

the growth conditions used in this study, 5 monolayer thick graphene does not form a continuous layer, so such thickness is not sufficient to completely cover the substrate.

1. Introduction

Epitaxial growth of graphene on SiC surfaces has been intensively studied lately as a promising route for obtaining highly reproducible and homogenous large-area material for electronic applications [1, 2, 3, 4, 5].

Graphene formation on SiC is the result of a complex process involving Si sublimation upon high temperature annealing of SiC in an inert atmosphere, leaving a carbon-rich surface whose mobile C atoms diffuse to self-assemble into ordered graphene layers [6]. The growth can be achieved under ultra-high vacuum [8] or, for increased domain sizes and structural quality, in an inert gas atmosphere [3, 9, 10, 11, 12] or disilane [12, 13] that helps to control the rate at which silicon sublimates and reduce the growth rate. Alternatively, growth can be achieved by using a confinement controlled sublimation method [14, 15] that limits the escape of Si and maintains a high Si vapour pressure. Here, the sublimed Si gas is confined in a graphite enclosure so that growth occurs near thermodynamic equilibrium.

Both non-equivalent faces of hexagonally stacked SiC $\{0\ 0\ 0\ 1\}$, namely the Si-face $(0\ 0\ 0\ 1)$ and the C-face $(0\ 0\ 0\ -1)$, have been used to obtain graphene, although the formation mechanism is different for the Si-terminated face compared to the C-terminated one.

On the Si-face of SiC the thickness of graphene layers is currently more controllable than on the C-face. Here, the growth initiates at step edges and proceeds in a layer-by-layer fashion, with 3 layers of SiC needed to sublime in order to form one graphene layer [25]. The first layer of graphene forms on top of the interfacial layer - the so-called $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ reconstruction that acts as a template for growth. The interfacial layer is topologically similar to

graphene, however it does not retain graphene's electronic properties, in particular it does not show graphene's characteristic linear dispersion and it is semiconducting in nature. Previous studies have shown that the homogeneity of this interfacial phase is influenced by the preparation procedure, however it remains unperturbed upon further graphitisation and it plays a critical role in the growth kinetics [16, 17]. The strong covalent bond of the interfacial layer with the underlying SiC substrate is responsible for the orientation of the reconstruction layer (30° rotation with respect to the substrate). This rotational orientation is further inherited by subsequent graphene layers although they only interact weakly by van der Waals forces with the interfacial layer [18].

In contrast to the Si-face, graphene growth on the C-face of SiC proceeds in a faster manner and it is more three-dimensional in nature, giving rise to graphene islands that have to grow relatively thick ($> 5\text{MLs}$) before a complete coverage is achieved [12, 20, 22]. Camara et al. show that the growth of graphene starts from defective sites, dislocations or point defects, that act as nucleation sites and that thin growth can be achieved by covering the SiC sample with a graphite cap that changes the Si sublimation rate [21]. The presence of a 'suboxide' (Si_2O_3) due to unintentional oxidation of the C-terminated face is an important factor known to inhibit graphene formation on the C-face, as reported by Srivastava et al. [12, 23].

In most cases reported so far, the growth on the C-face is generally inhomogeneous and it is not as well understood as that on the Si-face. For graphene formation on the C-face there is no distinct interfacial layer to act as a template, although STM studies observe 2×2 and 3×3 reconstructions at the interface between SiC and graphene [20]. The presence and absence of the buffer layer, as well as different surface reconstructions in the initial stages of graphitisation for

the Si-face compared to the C-face could possibly account for the difference in the growth modes on the two distinct faces.

Both experimental and theoretical evidence indicates that on the C-side the few layers graphene consist of rotationally disordered domains, misaligned with respect to the substrate, indicating though some preference for alignment relative to the substrate (layers rotated 30° , or $\pm 2.20^\circ$ with respect to the bulk SiC [10-10] direction) [18, 19]. The interaction between the first graphene layer and the underlying substrate is weak, allowing for a different orientation of the consequent graphene layers with respect to the substrate and the underlying graphene layers. This gives rise to turbostratic graphene containing rotational stacking faults that decouple adjacent graphene sheets, so that their electronic band structure is nearly identical to isolated graphene [19]. However, a recent study reveals the existence of distinct graphene grains with preferable azimuthal orientations instead of rotationally disordered graphene layers [11].

The absence of the interfacial layer and the weak coupling with the substrate gives rise to less electronic scattering for graphene formed on the C-face compared with that on the Si-face, resulting in lower carrier densities and higher carrier mobilities for the C-face graphene. Significantly higher carrier mobility (of up to ten times) of graphene monolayers grown on the C-terminated face compared to the Si-terminated one is the reason for which considerable effort has been directed recently towards better control of the growth on the C-face.

The current study is dedicated to exploring the growth of graphene on the C-face of SiC by studying its morphology, chemical composition and surface potential using a range of functional scanning probe microscopy, Raman spectroscopy and photoelectron spectroscopy techniques. The electronic uniformity of the surface has been probed by Scanning Kelvin Probe Microscopy (SKPM), which also provided information on sample morphology, as well as a

quantitative determination of the local thickness of graphene. These observations corroborated with Raman spectroscopy mapping were used to determine the quality of graphene and the size of crystallites. Useful insights into the chemical composition of the material studied were obtained using the XPS technique, which has furthermore validated the SKPM data.

2. Experimental details

Graphene was grown on nominally on-axis 4H SiC wafers with C-face surface terminations obtained from CREE. Samples were cleaned using the standard Radio Corporation of America (RCA) cleaning procedure prior to graphitisation. The graphene growth was carried out under highly isothermal conditions at a temperature of 2000 °C and at an ambient argon pressure of 1 atm. The growth conditions are as reported in detail in Ref. [11].

The morphology, structural and chemical properties as well as surface potential of the grown samples were investigated using Scanning Kelvin Probe Microscopy, Raman Spectroscopy and X-ray Photoelectron Spectroscopy.

Kelvin Probe Force Microscopy (KPFM) experiments were conducted in ambient conditions, on a Bruker Icon AFM, using Bruker highly doped Si probes (PFQNE-AL) with a force constant ~ 0.9 N/m. Frequency-modulated KPFM (FM-KPFM) technique operated in a single pass mode has been used in all measurements. FM-KPFM operates by detecting the force gradient (dF/dz), which results in changes to the resonance frequency of the cantilever. In this technique, an AC voltage with a lower frequency (f_{mod}) than that of the resonant frequency (f_0) of the cantilever is applied to the probe, inducing a frequency shift. The feedback loop of FM-KPFM monitors the side modes $f_0 \pm f_{\text{mod}}$ and compensates them by applying an offset DC voltage which is recorded to obtain a surface potential map. The spatial resolution of FM-KPFM

(<20 nm) as a result of detecting the electrostatic force gradient by the frequency shift is only limited by the diameter of the probe, since the force gradient is highly localized to the probe apex as a consequence of short-range detection [26, 27].

Raman maps of (10x10) μm^2 size were obtained using a Horiba Jobin-Yvon HR800 System. A 532 nm wavelength laser (2.33 eV excitation energy) was focused onto the sample through a 100x objective and data were taken with a spectral resolution of $(3.1 \pm 0.4) \text{ cm}^{-1}$ and XY resolution of $(0.4 \pm 0.1) \text{ cm}^{-1}$. The raw data were normalised with respect to the maximum of the TO phonon mode of 4H-SiC at $\sim 777 \text{ cm}^{-1}$.

X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos Axis Ultra DLD equipped with a magnetic immersion lens and operating in the hybrid mode. The X-ray source was an Al K_{α} anode operating at 15 kV and 5 mA, producing X-rays with an energy of 1486 eV which are monochromated with a quartz crystal before illuminating the sample. Survey spectra in the range from 1400 to -10 eV binding energy were taken with electron emission normal to the surface and with 160 eV analyser pass energy in the constant analyser transmission mode. Each analysis area was approximately $700 \times 300 \mu\text{m}$. Carbon (C1s) and silicon (Si2p) high-resolution narrow scans were also acquired at the same positions using 20 eV pass energy. CasaXPS software was used to measure the peak areas using a linear or Tougaard background, as appropriate, after correction using the NPL transmission function calibration [28] and using average matrix relative sensitivity factors (AMRSF) [29] to determine the concentrations of the detectable elements present.

3. Results and Discussion

3.1 Surface potential mapping

Samples prepared as described above have been characterised by KPFM and representative images are displayed in Figure 1, showing topography and surface potential data collected simultaneously from the same region of the sample.

Figure 1. Topography (a) and associated surface potential (b) image of graphene grown on the C-terminated face of 4H-SiC. Letters A-E denote areas of similar surface potential. (c) Histogram of the surface potential data corresponds to image presented in (b). Experimental data is fitted by 5 Lorentzian curves corresponding to areas A-E. High resolution topography (d) and surface potential (e) images of regions highlighted by white frames in (a) and (b), respectively.

As illustrated by Figure 1a, topography images show graphene domains that generally have either triangular or roughly hexagonal symmetry, indicating also the formation of one-dimensional graphene ridges. Ridges form to relieve compressive stress due to thermal

expansion mismatch between graphitic material and SiC and tend to occur along high-symmetry directions in the graphene lattice [24]. According to Hass et al. [6], the presence of ridges is thought to be related to structurally ideal graphene.

The electronic uniformity of the surface was probed by KPFM (Figure 1b). To date, KPFM has been successfully applied to quantitatively characterise and to assess the local graphene layer thickness in exfoliated and epitaxial graphene, see e.g. Refs. [30, 31, 32, 33, 34, 35].

As highlighted by the histogram in Figure 1c, the surface potential map (Figure 1b) displays a multi-modal potential distribution, showing regions with five main distinct surface potential contrast levels, denoted regions A, B, C, D, and E, respectively. Apart from A-like type features, all the other regions (B- to E-like) show clearly defined graphene domains with layer thickness increasing with the contrast level. So, if we assume that type B features (displaying the darkest level of contrast) correspond to one-layer graphene, the next consecutive graphene layer is given by type C features displaying a brighter contrast and showing a reduction in work function of $\sim (60 \pm 10)$ meV relative to B-like features. This value resulted from the analysis of multiple images on various regions of the sample. Similarly, type D- and type E-like regions appear with an even brighter contrast and could potentially be assigned to 3- and 4-layer thick graphene. Type D and type E features show a reduction in work function of $\sim (80 \pm 10)$ meV and $\sim (100 \pm 10)$ meV, relative to the preceding layer, respectively. On graphene grown epitaxially on 6H-SiC(0001), previous studies show a reduction in work function at the transition from bilayer to single layer graphene of 135 meV as measured in vacuum [28].

The A-like regions, which look significantly different from other graphene domains in Figure 2b, seem to be representative of this sample and other samples obtained under similar

growth conditions. A work function difference of (170 ± 10) meV is observed between A type and E type features. It is interesting to note that A type features seem to appear around triangular or trapezoidal shaped graphene islands of varying size ($\sim 0.1 - 0.5 \mu\text{m}$), highlighted by white arrows in topography and correspondingly in the associated surface potential map (Figures 1a and 1b). Such graphene islands, better visible in Figure 1c, seem to always form adjacent to SiC step edges and the line along their perimeter is topographically higher than the actual island.

3.2 Raman spectroscopy mapping

To elucidate the nature of A-type areas Raman mapping has been carried out. SKPM experiments have been performed first, then the sample has been transferred to the Raman system and the same area located for Raman mapping. Figure 2 shows topography, surface potential and Raman maps of the same area of the sample investigated in this work, with the experiments carried out on two different systems.

Figure 2: Topography (a) and surface potential maps (b) of a $(10 \times 10) \mu\text{m}^2$ area of the sample. Spatially resolved Raman spectroscopy maps of the area depicted in (a) and (b), corresponding to 2D, G and D peak intensity are shown in (c), (d) and (e), respectively. As guide to the eye, A-like feature highlighted by the white circle in (a) and (b) can be correspondingly identified on the Raman spectroscopy maps.

Raman maps presented in Figure 2 (*c, d, e*) are consistent with current SKPM observations of island-like morphology for graphene grown on the C-face. As highlighted by the surface potential map in Figure 2b, bright features (type A) observed previously can also be found in this region of the sample. These features correspond to black regions in the Raman maps. To correlate the above morphology observations with further details on the quality and thickness of the sample, representative spectra acquired at various distinct positions indicated on the Raman maps are presented in Figure 3 (*a, b*). Spectra corresponding to various graphene islands on the Raman maps are presented in Figure 3a and spectra obtained at the locations indicated by “*” symbols on the black regions on the Raman maps (equivalent to bright features, i.e. the A-type features in surface potential images) are shown in Figure 3b.

Figure 3: Representative Raman spectra recorded at various points on the surface showing the positions of the main bands associated with graphene: D, G, G^* , 2D superimposed over SiC bands. Spectra in (a) correspond to regions indicated by “ Δ ” symbols in Figure 2(c) (graphene islands in the Raman map) and spectra in (b) correspond to black areas on the Raman map (indicated by “*” symbols).

Raman spectra of graphene islands (denoted by “ Δ ” symbols): As illustrated in Figure 3a, Raman spectra display all modes typical to graphene, as well as the second order features of SiC in the range 1450 cm^{-1} to 1750 cm^{-1} .

The most prominent features in the Raman spectra of exfoliated monolayer graphene are: the G band at $\sim 1582\text{ cm}^{-1}$, the 2D (or G') band at $\sim 2700\text{ cm}^{-1}$ (for laser excitation of 2.41eV) and, depending on the structural integrity of the sample, the disorder-induced D band at $\sim 1350\text{ cm}^{-1}$ (for laser excitation of 2.41 eV) [36]. Both D and 2D bands exhibit dispersive behaviour and originate from a double resonance Raman process. Also appearing at $\sim 2460\text{ cm}^{-1}$ is the G^* mode associated with inter-valley scattering [36]. The G band is associated with the doubly

degenerate phonon mode at the center of the Brillouin zone and comes from a first order Raman scattering process in graphene.

For the sample studied here, as indicated in Figure 4 (a), the G band is centred at ~ 1576 cm^{-1} with small variations, indicating some degree of compressive strain of the sample.

Figure 4: (a) Positions of the G and 2D bands for individual graphene islands marked by “ Δ ” symbols in Figure 2. The correlated FWHM variations are shown in (b) and the crystallite size L_a in (c). All 3 graphs show values extracted from fitting individual peaks shown in Figure 3a.

The disorder-induced band due to surface dislocations, interaction with substrate, vacancies, etc., typically observed at around 1400 cm^{-1} is not very pronounced in the samples studied here. Based on the intensity ratio of D/G computed for spectra in Figure 3, the crystallite size L_a has been determined according to the following relationship [37]:

$$L_a [nm] = (2.4 \times 10^{-10}) \lambda_l^4 \left(\frac{I_D}{I_G}\right)^{-1}, \text{ where } \lambda_l \text{ is the laser wavelength in nanometer units.}$$

The crystallite size corresponding to sites denoted by “Δ” symbols, for $\lambda_l = 532$ nm, are plotted in Figure 4c. Relatively low D/G intensity ratio was found (as low as 0.03), indicating large crystallite size of up to 623 nm and overall consistent with high quality graphene.

Based on the 2D/G ratio and 2D lineshape, the identification of the number of layers in graphene samples obtained by mechanical exfoliation of graphite is generally straightforward. However, for graphene formed by all the other growth methods the 2D/G ratio is not a reliable thickness indicator anymore and the 2D lineshape and position have been used instead to derive information on the number of layers [36], stacking order [38], carrier mobility [36] and strain [39].

In our study, the 2D band peaks do not display any additional peak components and could be best fitted using a single Lorentzian component, suggesting turbostratic stacking, typical for graphene grown on the C-face of SiC [36]. Figure 4a indicates the position of the 2D peak after fitting with a Lorentzian. It is found that the actual position of 2D changes slightly from one location to another within the range $2690\text{--}2735\text{ cm}^{-1}$, with variations possibly due to graphene thickness non-uniformities. Variations in strain of a monolayer graphene can also give rise to changes in the 2D peak position, with values higher than bulk graphite ($\sim 2720\text{ cm}^{-1}$) being assigned to highly-strained epitaxial graphene [40, 45]. Highly strained graphene can be ruled out here, as generally the values found for 2D peak position are below 2720 cm^{-1} (only one point shows a higher value, at 2735 cm^{-1}).

We find that full-widths at half maximum (FWHM) for the 2D peak are in the range 45 to 85 cm^{-1} , which is likely to be due to (i) charge density broadening for few layer graphene and (ii) relaxation of the double resonance Raman selection rules associated with the random orientation

of the graphene layers with respect to each other [36]. In the case of epitaxial graphene, Raman studies show that the outcome is strongly dependent on the exact growth conditions and a large inconsistency of experimental results was reported. For example, for graphene grown epitaxially in ultra-high vacuum conditions, on the C-side of the SiC, Faugeras et al. found that the 2D band can be fitted by a single Lorentzian component, independent of the number of layers, with widths ranging from $\sim 60 \text{ cm}^{-1}$ for 5 - 10 layers thick graphene to $\sim 80 \text{ cm}^{-1}$ for a sample with 70 - 90 monolayers [41]. Contrary to these findings, a study of multilayer epitaxial graphene obtained by sublimation of a 4H-SiC (000-1) substrate in Ar atmosphere (i.e. growth conditions similar to the current study, except for lower annealing temperature of 1775°C and longer annealing time, of 60 mins) reports for 2D band widths of $\sim 28 \text{ cm}^{-1}$ for thick graphene samples, comparable to exfoliated graphene [42]. A few other studies of graphene formed on the C-terminated surface report a similar decrease in the full width at half maximum of individual 2D bands as the thickness of graphene stack increases [14, 43].

Nevertheless, consistent with previous studies, the fact that the Raman spectra of multilayer graphene on C-face resemble that of a monolayer signifies that domains of different thickness have similar electronic structure to that of a monolayer.

Raman spectra corresponding to A-type features (denoted by ‘*’ symbols): Raman spectra displayed in Figure 3b were recorded on black regions in the Raman maps (corresponding to A-type features on the surface potential maps) and do not show the presence of a 2D peak anymore, suggesting the absence of graphene in these regions. Furthermore, this suggests that for the growth conditions used in this study, the graphene islands should grow thicker than 5 monolayers to form a continuous layer and complete coverage of the substrate.

3.3 X-ray photoelectron spectroscopy studies

Further insights into chemical composition of the studied material were obtained using XPS technique. A straightforward analysis, assuming depth homogeneity, provides a mean composition of 75.9 at% carbon, 21.6 at% silicon, 2.3 at% oxygen, 0.2 at% vanadium[†] and 0.1 at% nitrogen. Later we analyse these results considering a layered structure, i.e. an inhomogeneous depth distribution of elements. The narrow scans, examples are shown in Figure 5, demonstrate that silicon is almost exclusively in a single chemical environment, which is consistent with the SiC at ~100.0 eV binding energy (Figure 5b).

Figure 5: (a) C1s and (b) Si2p core-level spectrum of graphene on the C-terminated SiC. Data is shown as points and the fit as a solid red line, components in the fit are shown as solid black and dotted lines. Note that the Si2p peak is a doublet due to spin-orbit coupling in the final state and both components are shown in the expected 1:2 intensity ratio. The spectra were fitted by a Gaussian-Lorentzian function after linear background subtraction. The typical positions for various chemical states are also indicated in the figure.

[†] The origin of vanadium in XPS spectra of the sample is not clear, as all samples grown at the same time and from the same wafer with the one presented in this study do not show the presence of this element.

Additionally, a small feature at higher binding energy is just visible and shown with a dotted line. It is unclear whether this is a separate component or simply asymmetry in the Si2p peak, however the binding energy position is close to that of the common laboratory contaminant polydimethylsiloxane (~102.0 eV), which may, therefore, form a trace part of a contaminant overlayer.

The C1s spectrum has more structure (Figure 5a), showing a peak at 282.6 eV binding energy (24.6% of C1s intensity), consistent with the silicon carbide substrate and a larger peak at 284.5 eV (44.6% of C1s) which is typical of sp^2 hybridised carbon. This second peak exhibits an extended tail to higher binding energy (lower kinetic energy), which might be attributed either to energy loss from the main sp^2 carbon peak or to organic contaminants. Under the assumption of a contaminant layer, the components in the peak fit in Figure 5a shown in dotted lines are based on binding energies typical of organic species, with peaks as indicated in Table 1:

Table 1: Components of the peak fit in Figure 5a

Binding energy	Organic species	% of C1s
285.0 eV	sp^3 hybridised carbon in hydrocarbon environment	21.0
285.7 eV	β -shifted carbon, constrained to be equal in area to carboxylate carbon	1.8
286.6 eV	carbon singly bound to oxygen, C-O	4.2
287.8 eV	carbonyl, C=O	2.0
289.0 eV	carboxylates, O=C-O	1.8

It should be noted that, if these features are due to the assigned functional groups, the presence of oxygen can be accounted for as belonging to the contaminant layer.

The compositions provided above assume that the material is homogenous in depth. This is clearly not the case, however the data can be used to estimate the average thickness of sp^2 hybridised carbon and contaminant layers on the sample. To do this, we use the straight-line approximation in which the photoelectron intensity diminishes exponentially with characteristic attenuation length, L . The value of L depends upon the kinetic energy of the photoelectrons and the material, however simple practical estimates have recently been published [46]. We assume that photoelectron diffraction effects from the SiC substrate are insignificant, as also confirmed by our previous studies. These assumptions and the densities of graphite and SiC are combined to construct a model for the XPS intensities in which three layers are considered: the SiC substrate, a layer of sp^2 carbon and an outer layer of contamination. There are four independent parameters which are altered to provide a unique solution to the XPS data, namely: the substrate composition (x in $Si_xC_{(1-x)}$), the contaminant layer composition (y in $C_{(1-y)}O_y$), the thickness of sp^2 carbon (t_1) and the thickness of the contaminant layer (t_2). The composition of the SiC substrate depends upon the relative C1s and Si2p intensities shown in Figure 5 and the overlayer thicknesses (t_1 and t_2), which attenuate the C1s photoelectrons more quickly than the higher kinetic energy Si2p photoelectrons. The composition of the substrate is found to be $x = 51$ at% of silicon, very close to the expected value. The thickness of the sp^2 layer, t_1 , which includes graphene, is found to be 1.7 nm and the contaminant layer thickness, $t_2 \approx 0.9$ nm. The overlayer composition resulted in $y = 10$ at% oxygen, which is not unreasonable given the C1s peak fit shown in Figure 5a. Within the peak fit, there is a strong correlation between the sp^2 and sp^3 intensities as well as some uncertainty in the assignment of the higher energy peaks shown by

dotted lines in Figure 5a. Therefore, estimation of the individual thicknesses of the two layers is rather difficult. However, the combined average thickness of all carbonaceous overlayers, $t_1+t_2 \approx 2.6$ nm, is more certain and should be accurate to within 10% relative error. Non-homogeneity of overlayer thickness will result in an underestimation of the average thickness by XPS, but this will not introduce a significant ($> 10\%$) error unless the non-uniformity is extreme, *i.e.* similar in magnitude to the film thickness itself.

It is noteworthy that, if we consider that the sp^2 layer consists entirely of graphene, the determined thickness of the sp^2 layer ($t_1=1.7$ nm) would correspond to 5 graphene layers, which is in precise agreement with SKPM observations presented earlier in the paper.

4. Conclusions

A study of morphology, chemical composition and surface potential of graphene grown on the C-face of SiC is presented in this paper. Surface potential maps revealed that the growth consists of 2D graphene islands of varying lateral size and provided a quantitative characterisation of the local graphene layer thickness. Consistent with SKPM observations, Raman spectroscopy mapping supports the island-like morphology for graphene grown on the C-face. High quality graphene and large area crystallites of up to 620 nm are found based on the Raman spectroscopy data. A comprehensive chemical analysis of the sample has been provided by XPS investigations, with the number of graphene layers consistent with that determined by surface potential mapping.

Based on the above observations, it can be summarised that on the C-terminated face, graphene growth proceeds in an island-like fashion rather than in a layer-by-layer manner as established on the Si-terminated face of SiC. It is observed that even when patches of graphene are 5 layers thick, there are still some exposed areas ($\sim$ up to 25% on a $10 \times 10 \mu m^2$) of bare SiC. This

suggests a different growth mechanism on the C-terminated face compared to the Si-face. The growth on the C-face is consistent with Volmer-Weber growth mode for thin films [47], where initial growth occurs at a large number of nucleation sites (indicated by white arrows in Figure 1), leading to the formation of 2D islands in the following phase. As expected, these nucleation sites are always located at defects, i.e. substrate steps or polishing lines on the substrate (better visible on the surface potential maps in Figure 1b). It has been observed by a previous study that on the C-face growth is initiated at by threading screw dislocations in the SiC substrate, which act as preferred nucleation sites [48]. Under vacuum conditions, several groups reported graphene growth both through island formation [21, 23] as well as growth of relatively thick films (up to 15 ML average thickness in [12]) that uniformly cover the substrate. Under Ar atmosphere (i.e. similar to the current study, although at lower temperatures) graphene grown on the C-face also reveals the formation of thick and isolated graphene islands, which, however, do not necessarily coalesce and form a continuous layer [12, 22].

The variation in size of the islands, as illustrated in Figure 1 of this study, is furthermore consistent with the Volmer-Weber growth. We also find that the islands have to grow relatively thick, as a 5-monolayer thickness is not sufficient to achieve a complete coverage of the substrate.

With the particular conditions used for graphene growth in the current study and considering that the Volmer-Weber mode is dominant, synthesising large-scale monolayer graphene on C-face of SiC remains a challenge. Optimisation of growth conditions, perhaps by using a different gas atmosphere, is required for uniform monolayer growth, in order to benefit from the higher carrier mobility of graphene on the C-face compared to the Si-face.

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Figure and Table captions:

Figure 1. Topography (a) and associated surface potential (b) image of graphene grown on the C-terminated face of 4H-SiC. Letters A-E denote areas of similar surface potential. (c) Histogram of the surface potential data corresponds to image presented in (b). Experimental data is fitted by 5 Lorentzian curves corresponding to areas A-E. High resolution topography (d) and surface potential (e) images of regions highlighted by white frames in (a) and (b), respectively.

Figure 2: Topography (a) and surface potential maps (b) of a $(10 \times 10) \mu\text{m}^2$ area of the sample. Spatially resolved Raman spectroscopy maps of the area depicted in (a) and (b), corresponding to 2D, G and D peak intensity are shown in (c), (d) and (e), respectively. As guide to the eye, A-like feature highlighted by the white circle in (a) and (b) can be correspondingly identified on the Raman spectroscopy maps.

Figure 3: Representative Raman spectra recorded at various points on the surface showing the positions of the main bands associated with graphene: D, G, G^* , 2D superimposed over SiC bands. Spectra in (a) correspond to regions indicated by “ Δ ”

symbols in Figure 2(c) (graphene islands in the Raman map) and spectra in (b) correspond to black areas on the Raman map (indicated by “*” symbols).

Figure 4: (a) Positions of the G and 2D bands for individual graphene islands marked by “Δ” symbols in Figure 2. The correlated FWHM variations are shown in (b) and the crystallite size L_a in (c). All 3 graphs show values extracted from fitting individual peaks shown in Figure 3a.

Figure 5: (a) C1s and (b) Si2p core-level spectrum of graphene on the C-terminated SiC. Data is shown as points and the fit as a solid red line, components in the fit are shown as solid black and dotted lines. Note that the Si2p peak is a doublet due to spin-orbit coupling in the final state and both components are shown in the expected 1:2 intensity ratio. The spectra were fitted by a Gaussian-Lorentzian function after linear background subtraction. The typical positions for various chemical states are also indicated in the figure.

Table 1: Components of the peak fit in Figure 5a