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High Quality Epitaxial Graphene by Hydrogen-etching of 3C-SiC(111) thin-film on Si(111)

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Abstract

Etching with atomic hydrogen as a preparation step before the high-temperature growth process of graphene onto a thin 3C-SiC film grown on Si(111) greatly improves the structural quality of topmost graphene layers. Pit formation and island coalescence, which are typical of graphene growth by SiC graphitization, are quenched and

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accompanied by widening of the graphene domain sizes to hundreds of nm, and by a significant reduction in surface roughness down to a single substrate bilayer. The surface reconstructions expected for graphene and the underlying layer are shown with atomic resolution by scanning tunnelling microscopy (STM). Spectroscopic features typical of graphene are measured by core-level photoemission and Raman spectroscopy.

Introduction

The integration of graphene into devices of modern and future electronics will be a trade-off between the benefits offered by its promising properties and the associated costs for development and production of this unique material.¹ Currently, there are several methods for producing graphene flakes of various dimensions, shape and quality, each method having a particular associated cost for mass production.^{1,2} Graphitization of silicon carbide is an attractive choice,³ its main advantage being that graphene layers are formed directly on a semiconductor substrate and do not require any transfer steps for subsequent device processing. Heating SiC to temperatures between 1200°C and 1400°C in ultra-high-vacuum (UHV), or above 1600°C in inert atmosphere,⁴ causes Si atoms to desorb from the surface,⁵ and the remaining carbon atoms may rearrange to form graphene as the topmost layer.^{6–10} This reaction occurs on various hexagonal polytypes of SiC, and differences in the reconstructed layer are observed when the the experiment is performed on silicon *vs.* carbon terminated faces of SiC(0001).^{6,11,12} On the Si-terminated surface sublimation of silicon atoms from the step edges generates a carbon-rich surface reconstruction, also known as the buffer layer. The C buffer layer and the underlying SiC substrate present an electronic structure different from that of pure graphene,^{7,13,14} which can be formed above the buffer layer with further annealing.

Since single-crystal SiC remains substantially more expensive than pure silicon, the growth of graphene from thin layers of cubic SiC grown on Si has been proposed as a way to limit production costs.^{15–17} Other options have been explored, like the growth by CVD

on 3C-SiC/Si.^{18,19} However, growing thin-films of cubic-SiC over silicon wafers by chemical vapor deposition (CVD) looks the simplest way to exploit existing silicon-based production lines for electronics.²⁰ Graphene synthesis on Si-terminated 3C-SiC(111) thin-films on Si(111) has been recently demonstrated, by heating in UHV at temperatures ranging from 600°C to 1300°C.^{16,21,22} Improved surface quality and morphology of the graphene layer was achieved by polishing the crystal prior to the annealing experiment.²³

Improvements to the atomic-scale morphology and roughness are still desired. Hydrogen etching has been proven to be an effective tool for obtaining high-quality SiC surfaces,^{24,25} and this could lead to higher-quality buffer and topmost graphene layers.^{26,27} In this work, we combine the previously demonstrated surface polishing technique with monoatomic H-etching of the substrate before final annealing for producing graphene on 3C-SiC thin-films on Si(111). By using a complementary set of characterization techniques, including Scanning Tunneling Microscopy (STM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, we demonstrate a definite improvement of the graphene layers at the atomic scale, and an increase of the typical domain size by almost one order of magnitude, with a significant reduction in roughness down to monolayer step size.

Experimental

The graphene growth was performed on a Si-terminated 1 μm thick 3C-SiC(111) film deposited on p-doped ($\rho = 1 - 10 \Omega \cdot \text{cm}$) Si(111) wafer, which was subsequently chemically and mechanically polished (NOVASiC - France). The as-received wafer was cut into a $13 \times 3 \text{ mm}^2$ size, and was cleaned ex-situ by sequential 10 min. sonication steps at 50 °C in isopropyl alcohol, deionized water and acetone. The sample was subsequently inserted into a UHV chamber (base pressure $1 \times 10^{-11} \text{ mbar}$) and degassed at 600 °C for several hours by direct current heating. The substrate was then heated to 1000 °C in a monoatomic hydrogen environment ($7.5 \cdot 10^{-6} \text{ mbar}$) for 15 minutes in order to remove the majority of the native oxide

species from the surface and to form a carbon-rich superstructure. The atomic hydrogen was produced by thermal cracker (EFM-H, ScientaOmicron), fed with ultra-pure hydrogen gas through a leak valve. The sample was cooled down to room temperature while the pressure recovered to base value of $5 \cdot 10^{-11}$ mbar. Finally, an annealing process at 1250 °C for 10 minutes in an overall pressure better than 3.3×10^{-9} mbar was used to produce graphene on the surface. For comparison, an alternate graphene growth procedure was also investigated, whereby the the monoatomic hydrogen etching step was replaced by an annealing step at 950 °C for 10 minutes in UHV.

The sample chemistry was investigated by XPS, using 300 W source of unmonochromatized Mg K α radiation (1253.6 eV) (DAR 400, ScientaOmicron). The photoelectrons were collected at a take-off angle of 70° by a hemispherical electron energy analyzer (SPHERA II with a 7 channel detector, ScientaOmicron). The angle between the source and analyser is 65°, and the overall experimental resolution is 1 eV. The morphology and the quality of the graphene grown by the methods described above were investigated *in-situ* by means of STM (VT STM/XA, ScientaOmicron) at room temperature in constant current mode with a W etched tip, and *ex-situ* by Raman spectroscopy (inVia Renishaw Raman Microscope) at room temperature and atmospheric pressure, using an excitation laser wavelength of 532 nm.

Results and Discussion

The evolution of the surface chemistry at each of the different steps during the sample preparation was tracked by XPS, as shown in Fig. 1. The as-received sample principally comprises carbon and silicon, identified by the presence of C 1s, Si 2s and Si 2p peaks, though a significant quantity of oxygen (O 1s) is also observed. After degassing at 600 °C in UHV, only a small amount of oxygen is removed. Annealing at 1000 °C in presence of atomic H significantly reduces the O content. The atomic H exposure is found to improve

the surface sample quality (see below), however annealing at high temperature in vacuum also reduces the O contamination (see SI). Annealing at 1250 °C in UHV leads to graphene formation in all cases.

Room temperature STM measurements were performed in order to assess the morphology of the graphene including of microscopic defects, roughness, domain size and shape. In Figure 2c it is evident that the surface prepared without H-treatment has small flat areas but presents irregularly-shaped steps and residual nm-sized pits and islands.

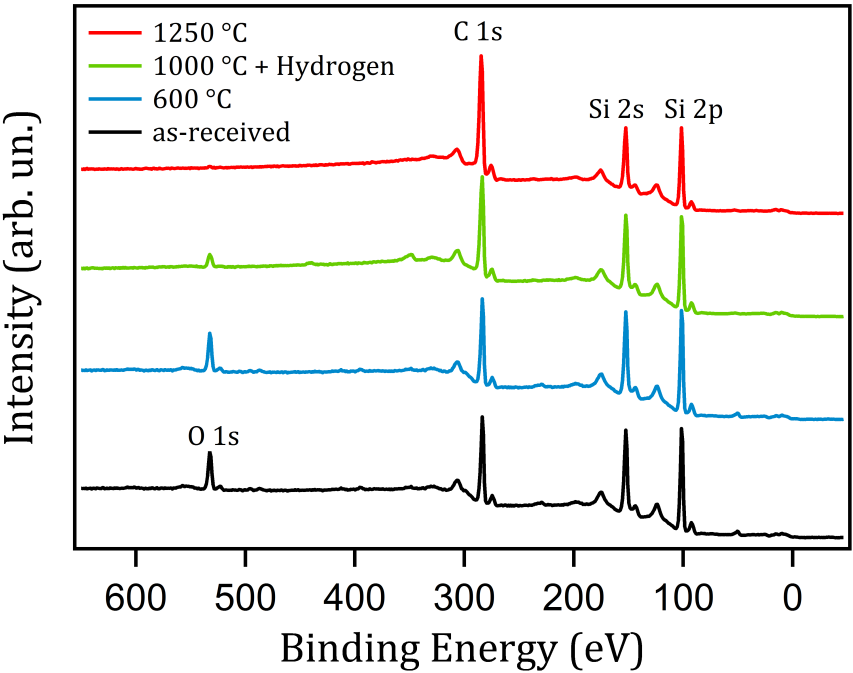


Figure 1: XPS survey of 3C-SiC(111)/Si(111) after different annealing steps, from the as-received sample at room-temperature to the graphene layer at 1250°C, assisted by atomic hydrogen exposure at 1000°C. Spectra are vertically stacked for clarity.

By contrast, the H-treated sample shown in Figure 2a has no pits or islands, and we can clearly see large regular terraces almost one order of magnitude wider than on the non-etched surface. The remaining triangular shape of the surface features reflects the anisotropic in-plane growth rates of the fcc(111) faces of SiC over Si(111), and represents the grain structure of the SiC film rather than the morphology of the graphene overlayer.^{21,28} The action of H in the treatment of SiC thin-films on Si has been explained as modifying

the terrace dynamics, favouring lateral sublimation of Si from the step edges over vertical sublimation from the terraces (the latter effect being ascribed to pit formation). This favours a more uniform Si sublimation and widening of the terrace.^{5,26} The improvement of the surface quality on the H-etched substrate can be appreciated by comparing the line profiles of panels b) and d), respectively. We note the complete suppression of the formation of pits, as the surface is completely covered by homogeneous terraces that are only a single SiC bilayer step apart (panel b). The average surface roughness **calculated on a 100x100 nm² area** is reduced from 3.7 to 0.7 Å by using the hydrogen treatment.

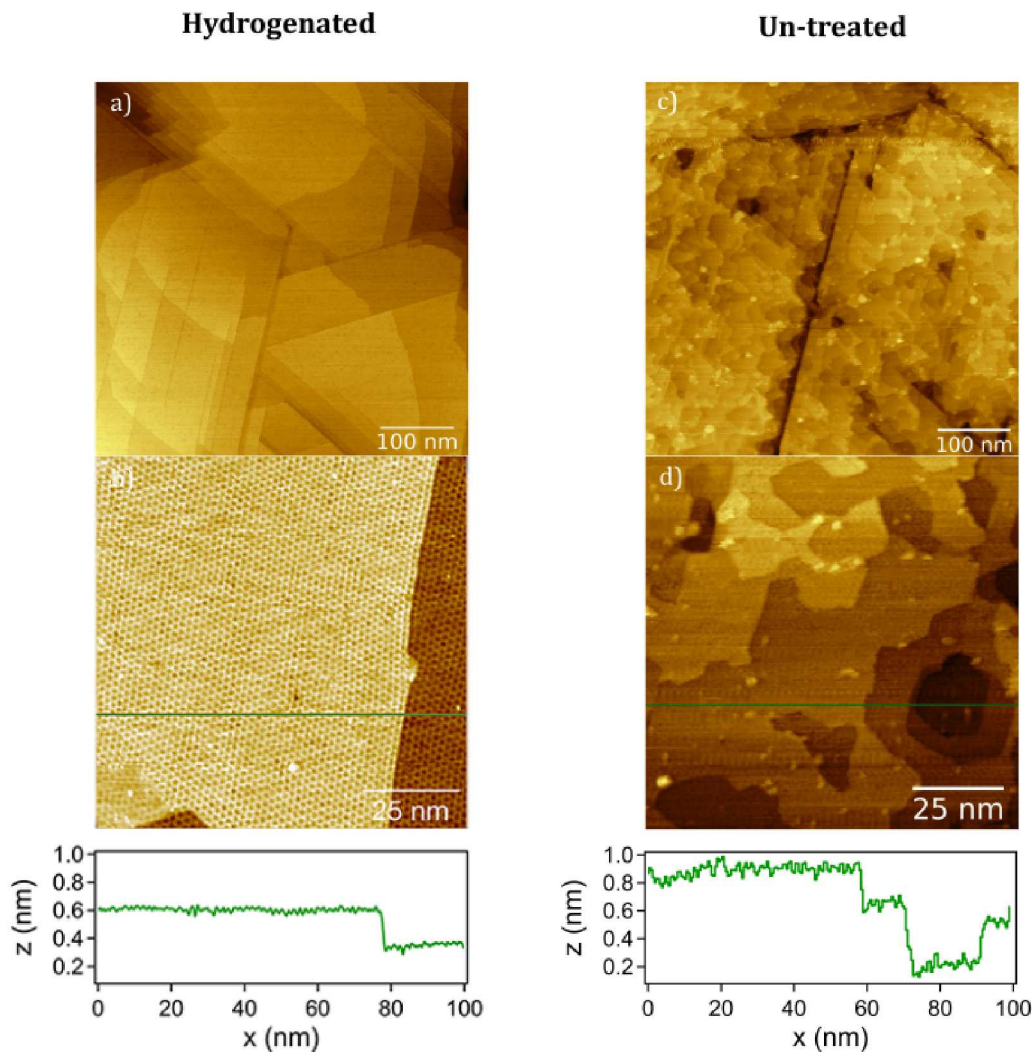


Figure 2: STM images acquired on graphene grown at 1250 °C on H-etched and untreated SiC, taken on different scales: upper images ($500 \times 500 \text{ nm}^2$), bottom images ($100 \times 100 \text{ nm}^2$). In the bottom panels, line profiles on both H-treated and untreated samples. STM parameters: a) (-1.4 V, 2 nA), b) (-2 V, 0.7 nA), c) (-1.7 V, 1.8 nA) and d) (-1.7 V, 1.8 nA).

The beneficial effects of the hydrogen treatment can be also appreciated by the inspection of STM images acquired at higher resolution. Figure 3a shows atomic details of the $(6\sqrt{3} \times 6\sqrt{3})R 30^\circ$ structure,²⁹ which is present underneath the graphene and buffer layer, along with the presence of some lattice defects and vacancies. This structure arises from the buffer layer, and is visible by STM on well-prepared few-layer graphene surfaces.^{29,30} The regular (6×6) moiré structure is clearly visible in Figure 3b.

The combined presence of the (6×6) moiré and of the $(6\sqrt{3} \times 6\sqrt{3})R 30^\circ$ reconstructions in

the STM images after the final annealing of the H-etched SiC are the proof of the presence of a well-formed graphene layer, though the overall thickness must be assessed by other techniques.³¹

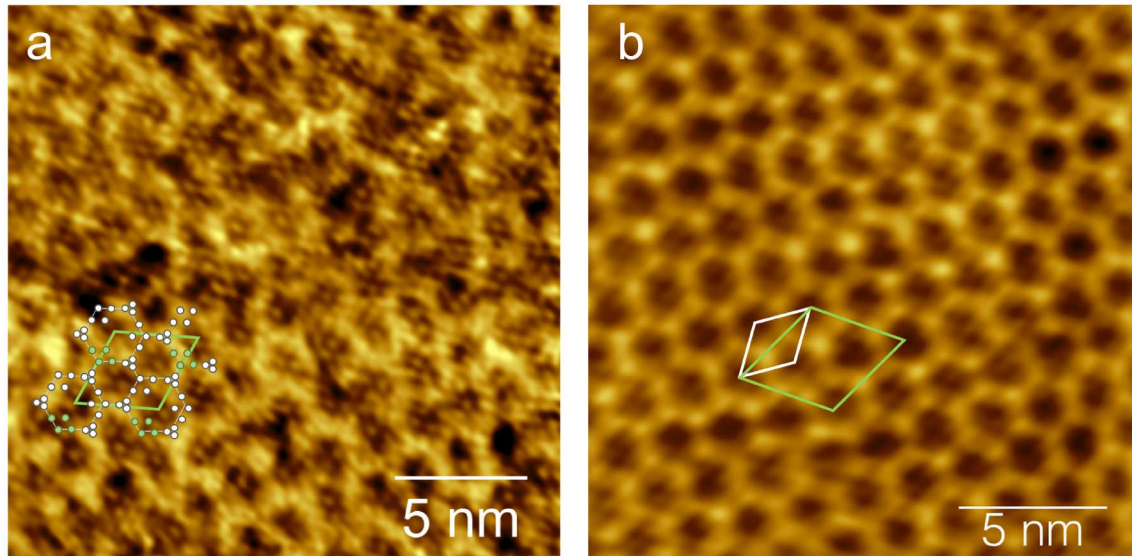


Figure 3: High resolution STM images of the SiC surface after H-etching and annealing at 1250 °C for graphene growth. Panel a): image acquired at $V_{bias} = -0.7V$, $I_{tip} = 1.2$ nA; in these conditions it is possible to see the details of the $(6\sqrt{3} \times 6\sqrt{3})R 30^\circ$ reconstruction (depicted around the unit cell marked by a green rhombus) present underneath the top graphene surface; a schematic drawing²⁹ is superimposed to the image. Panel b): image acquired at $V_{bias} = -2.0V$, $I_{tip} = 0.7$ nA; in this image, the 6×6 reconstruction (white rhombus) is clearly visible.

The spectroscopic profile of the carbon 1s core-level can be used to fingerprint of the chemical coordination of C in graphene-related compounds.^{32,33} The C 1s spectra of the graphene layers formed with and without the H-etching procedure are shown in Fig. 4. The spectra exhibit a multiple-component shape, as expected for graphene growth on SiC,^{6,21,31,34} which are associated to graphene (G), to the underlying SiC and to the carbon buffer layer (B). A quantitative evaluation is obtained by a curve fitting with pseudo-Voigt functions, using a linear combination of equally weighted Lorentzian and Gaussian curves, taking into account the asymmetric character of the peak related to graphene ($\alpha = 0.15 \pm 0.05$). In the H-treated sample, the graphene peak is at a binding energy (BE) of 284.6 eV, the B peak at 285.7 eV and the SiC component at 283.4 eV; analogous BE values within the experimental

uncertainties are determined for the non H-treated sample (Table 1). All the components are in agreement with previous experiments performed on both cubic^{21,31} and hexagonal SiC substrates,^{6,34} thus the H-treatment does not affect the chemistry of graphene formation.

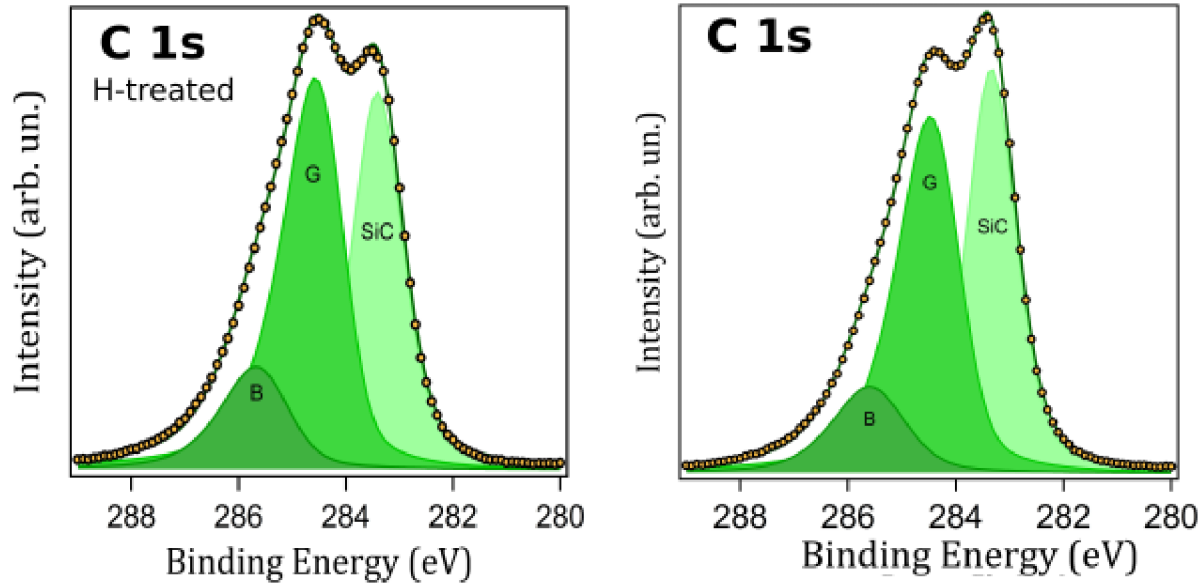


Figure 4: C 1s XPS spectra for graphene growth in UHV at 1250 °C for both hydrogen-treated (left) and un-treated (right) samples. The three different features can be attributed to the substrate (SiC), buffer layer (B) and graphene (G). Experimental data (open dots) and results of the fitting analysis: sum fitting curve (continuous line), and the three fitting components (coloured peaks).

From the attenuation of the C 1s core-level component related to SiC with respect to B and G,³¹ we estimate an average number of 4.0 nominal graphene layers for the un-treated sample and 4.6 for the hydrogenated one, but this apparent increase can be related to a lower activation barrier for the growth, which is correlated with the smoothness of the H-treated sample surface.

The introduction of the monoatomic hydrogen etching step before graphene formation leads to more efficient Si sublimation.²⁶ As such, the growth of the G component initiates at lower annealing temperatures than for the non H-treated sample. At ≈ 1000 °C the G-related peak emerges for the H-treated sample, which is not the case for the untreated sample (see SI). This evidence suggest that the hydrogenation step leaves a more uniform buffer layer to

Table 1: Fit results for the C 1s XPS spectrum of the the hydrogen-treated and the untreated samples. Binding energy (BE) position (± 0.2 eV), full-width at half-maximum (FWHM), and relative intensity (peak areas).

| Sample | Peak Component | BE (eV) | FWHM (eV) | Area (%) |
|------------|----------------|---------|-----------|----------|
| H-treated | G | 284.6 | 1.5 | 48 |
| | B | 285.7 | 1.6 | 14 |
| | SiC | 283.4 | 1.1 | 38 |
| un-treated | G | 284.4 | 1.5 | 44 |
| | B | 285.6 | 1.6 | 13 |
| | SiC | 283.3 | 1.1 | 43 |

seed graphene growth.

Raman spectroscopy is a well established tool for determining the graphene quality, the influence of the substrate interaction via strain and defects, and to estimate the number of graphene layers on a sample.^{35,36}

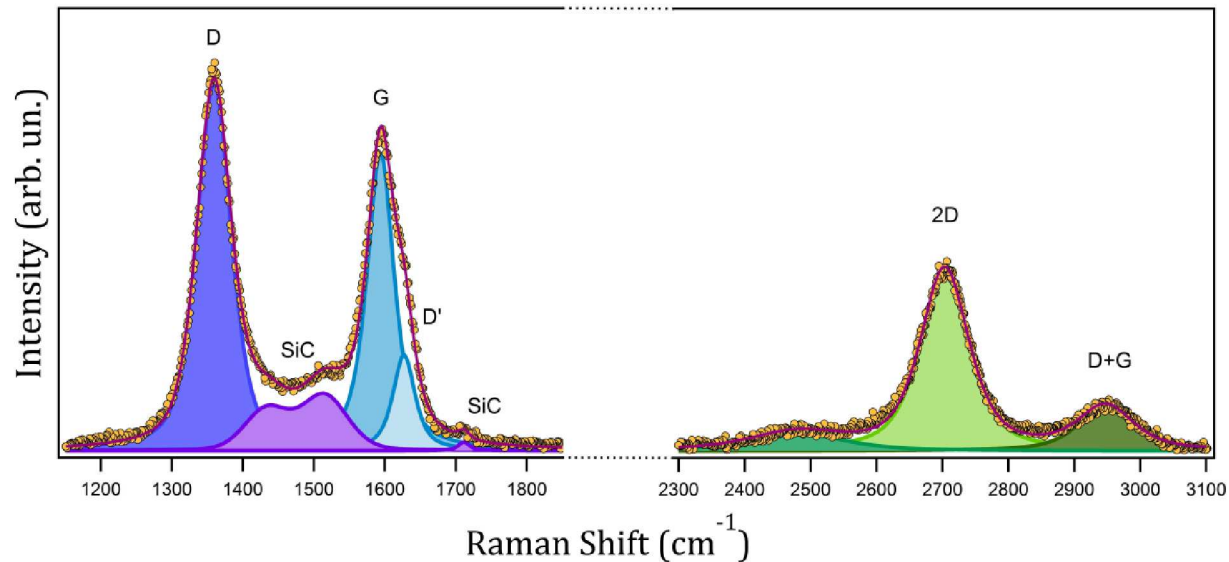


Figure 5: Raman bands of graphene grown after monoatomic Hydrogen etching. **Only a linear background was subtracted to the Raman data.** The G and 2D bands, typical of graphene, are clearly visible: in particular, G-band arises from the stretching of the C-C bond in graphitic materials that have in common the sp^2 hybridization. The D-band and D' shoulder are caused by defects in the structure of graphene, typically observed for graphene grown with similar methods. **SiC peaks** are features arising from the substrate, according to previous studies.^{35,37,38} The D+G band requires no defects for its activation, since it originates from a process where momentum conservation is satisfied by two phonons with opposite wavevectors. Through the analysis of the fitting results contained in Table 2 it is possible to determine the overall graphene quality.

In Figure 5 we show the Raman spectrum of the graphene sample grown at 1250 °C with H-etching. Four main peaks and one shoulder are observed and fitted with Lorentzian curves, at positions of 1359.3 cm^{-1} (D), 1594.0 cm^{-1} (G), 1627.0 cm^{-1} (shoulder D'), 2703.4 cm^{-1} (2D) and 2946.8 cm^{-1} (D+G). Small contributions from the substrate are also visible, labelled as SiC.^{37,39} The G and 2D bands are strictly related to the graphene layer/s quality. The position of the G-band is in very good agreement with previous measurements of graphene grown on SiC bulk substrates,^{39–41} confirming unequivocally the presence of graphene on the thin SiC films. The G band is blue-shifted from that of micromechanically-cleaved graphene,⁴² and is very close to that of monolayer graphene on SiC.³⁹ However, the position of the band cannot be straightforwardly correlated to the number of layers, inasmuch it also depends on the interaction between graphene and the supporting substrate,⁴⁰

as well as the strain inherent in the epitaxial confinement and on the graphene doping.⁴³ The width of the 2D band (88 cm^{-1}) is inversely correlated to the number of layers, but is heavily influenced by defects, vacancies, strain and doping,^{43–45} as has also been observed for graphene grown on hexagonal polytypes of bulk SiC.⁴⁰ The presence of strain, vacancies and defects has an overwhelming influence on the width of the 2D band, far surpassing the contribution related to the number of G layers. Neglecting these leads to an overestimation of the number of graphene layers,⁴⁰ whereby the estimate by XPS should be more reliable. The high number of dislocations in the thin epitaxial SiC film prepared on Si, is expected to contribute to a higher density of defects in graphene with respect to the growth on bulk SiC. This is indirectly confirmed by the relatively high D/G ratio in the Raman spectrum (Fig. 5) and by the STM image shown in Fig. 3a. We notice that Raman is very sensitive to local defects in the single hexagonal rings which cause peak D, even in presence of large ordered graphene lattice domains as imaged by STM. We remark that the D/G ratio in the H-treated sample is lower by about 15% with respect to the untreated sample (see Fig. 3 of the Supplementary Information), and there is a reduction of the D' shoulder, both associated to an improvement of the final graphene quality after hydrogenation of the SiC thin-film substrate. Overall, the Raman fingerprint of our sample confirms the formation of good quality graphene, similar to that obtained on polished samples in Ref.²³ However, Raman does not provide a full account of the improvement in the surface quality shown by STM, indicating that edge defects at the dislocations are affecting heavily its sensitivity to surface quality, and to the beneficial effect of H etching.

Table 2: Fit results of the Raman spectra of the hydrogenated sample.

| | Position (cm^{-1}) | FWHM (cm^{-1}) | Area (arb. un.) |
|----------|-------------------------------|---------------------------|-----------------|
| D band | 1359.3 | 58 | 4195 |
| G band | 1594.0 | 46 | 2925 |
| D' band | 1627.0 | 37 | 761 |
| 2D band | 2703.4 | 88 | 3422 |
| D+G band | 2946.8 | 100 | 871 |

Conclusions

In conclusion, we have performed a detailed analysis of the effect of atomic H-etching on the 3C-SiC thin-films on Si(111) substrate, for graphene grown by high temperature annealing. We find superior quality of graphene after etching the SiC substrate at 1000 °C in atomic H atmosphere (10^{-5} Torr) before the final annealing at 1250 °C. The STM images show a substantial improvement of the morphology when the H-etching is used, showing pit-free large (hundreds of nm) and flat (single layer steps) terraces of graphene with a clear (6×6) moiré pattern coupled to a $(6\sqrt{3}\times 6\sqrt{3})R\ 30^\circ$ reconstruction. Raman spectra confirm the good quality of the graphene layers, and point to the presence of unavoidable strain effects. In summary, H-etching is an excellent method for obtaining high quality graphene surfaces on SiC. While XPS and Raman spectroscopy are essential tools for probing the overall quality of graphene, STM is an extremely powerful technique for providing detailed surface information, required for determine the subtle differences in graphene quality at the atomic scale.

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Supporting Information Available

In the Supporting Information we report: survey XPS spectra of both H-treated and untreated samples at lower annealing temperatures, with corresponding high-resolution C 1s data and fittings, and Raman spectroscopy data taken on untreated sample.

References

1. Novoselov, K. S.; Fal, V.; Colombo, L.; Gellert, P.; Schwab, M.; Kim, K. A roadmap for graphene. *Nature* **2012**, *490*, 192–200.
2. Ferrari, A. C.; Bonaccorso, F.; Fal'Ko, V.; Novoselov, K. S.; Roche, S.; Bøggild, P.; Borini, S.; Koppens, F. H.; Palermo, V.; Pugno, N. *et al.* Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems. *Nanoscale* **2015**, *7*, 4598–4810.
3. Berger, C.; Song, Z.; Li, T.; Li, X.; Ogbazghi, A. Y.; Feng, R.; Dai, Z.; Marchenkov, A. N.; Conrad, E. H.; First, P. N. *et al.* Ultrathin epitaxial graphite: 2D electron gas properties and a route toward graphene-based nanoelectronics. *The Journal of Physical Chemistry B* **2004**, *108*, 19912–19916.
4. Emtsev, K. V.; Bostwick, A.; Horn, K.; Jobst, J.; Kellogg, G. L.; Ley, L.; McChesney, J. L.; Ohta, T.; Reshanov, S. A.; Röhl, J. *et al.* Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide. *Nature Materials* **2009**, *8*, 203–207.
5. Sun, G.; Liu, Y.; Rhim, S.; Jia, J.; Xue, Q.; Weinert, M.; Li, L. Si diffusion path for pit-free graphene growth on SiC (0001). *Physical Review B* **2011**, *84*, 195455.
6. Emtsev, K. V.; Speck, F.; Seyller, T.; Ley, L.; Riley, J. D. Interaction, growth, and ordering of epitaxial graphene on SiC(0001) surfaces: A comparative photoelectron spectroscopy study. *Phys. Rev. B* **2008**, *77*, 155303.

7. Lauffer, P.; Emtsev, K. V.; Graupner, R.; Seyller, T.; Ley, L.; Reshanov, S. A.; Weber, H. B. Atomic and electronic structure of few-layer graphene on SiC(0001) studied with scanning tunneling microscopy and spectroscopy. *Phys. Rev. B* **2008**, *77*, 155426.
8. Riedl, C.; Coletti, C.; Starke, U. Structural and electronic properties of epitaxial graphene on SiC(0001): a review of growth, characterization, transfer doping and hydrogen intercalation. *Journal of Physics D: Applied Physics* **2010**, *43*, 374009.
9. Sutter, P. Epitaxial graphene: How silicon leaves the scene. *Nature Materials* **2009**, *8*, 171–172.
10. Robinson, J.; Weng, X.; Trumbull, K.; Cavalero, R.; Wetherington, M.; Frantz, E.; LaBella, M.; Hughes, Z.; Fanton, M.; Snyder, D. Nucleation of Epitaxial Graphene on SiC(0001). *ACS Nano* **2010**, *4*, 153–158.
11. Kusunoki, M.; Suzuki, T.; Hirayama, T.; Shibata, N.; Kaneko, K. A formation mechanism of carbon nanotube films on SiC(0001). *Applied Physics Letters* **2000**, *77*, 531–533.
12. Forbeaux, I.; Themlin, J.-M.; Charrier, A.; Thibaudau, F.; Debever, J.-M. Solid-state graphitization mechanisms of silicon carbide 6 H - SiC polar faces. *Applied Surface Science* **2000**, *162–163*, 406 – 412.
13. Varchon, F.; Feng, R.; Hass, J.; Li, X.; Nguyen, B. N.; Naud, C.; Mallet, P.; Veuillen, J.-Y.; Berger, C.; Conrad, E. H. *et al.* Electronic Structure of Epitaxial Graphene Layers on SiC: Effect of the Substrate. *Phys. Rev. Lett.* **2007**, *99*, 126805.
14. Goler, S.; Coletti, C.; Piazza, V.; Pingue, P.; Colangelo, F.; Pellegrini, V.; Emtsev, K. V.; Forti, S.; Starke, U.; Beltram, F. *et al.* Revealing the atomic structure of the buffer layer between SiC(0 0 0 1) and epitaxial graphene. *Carbon* **2013**, *51*, 249 – 254.
15. Aristov, V. Y.; Urbanik, G.; Kummer, K.; Vyalikh, D. V.; Molodtsova, O. V.; Preobrajenski, A. B.; Zakharov, A. A.; Hess, C.; Hänke, T.; Büchner, B. *et al.* Graphene

- Synthesis on Cubic SiC/Si Wafers. Perspectives for Mass Production of Graphene-Based Electronic Devices. *Nano Letters* **2010**, *10*, 992–995, PMID: 20141155.
16. Ouerghi, A.; Kahouli, A.; Lucot, D.; Portail, M.; Travers, L.; Gierak, J.; Penuelas, J.; Jegou, P.; Shukla, A.; Chassagne, T. *et al.* Epitaxial graphene on cubic SiC(111)/Si(111) substrate. *Applied Physics Letters* **2010**, *96*.
17. Suemitsu, M.; Fukidome, H. Epitaxial graphene on silicon substrates. *Journal of Physics D: Applied Physics* **2010**, *43*, 374012.
18. Michon, A.; Vézian, S.; Ouerghi, A.; Zielinski, M.; Chassagne, T.; Portail, M. Direct growth of few-layer graphene on 6H-SiC and 3C-SiC/Si via propane chemical vapor deposition. *Applied Physics Letters* **2010**, *97*, 171909.
19. Portail, M.; Michon, A.; Vézian, S.; Lefebvre, D.; Chenot, S.; Roudon, E.; Zielinski, M.; Chassagne, T.; Tiberj, A.; Camassel, J. *et al.* Growth mode and electric properties of graphene and graphitic phase grown by argon–propane assisted {CVD} on 3C–SiC/Si and 6H–SiC. *Journal of Crystal Growth* **2012**, *349*, 27 – 35.
20. Nishino, S.; Powell, J. A.; Will, H. A. Production of large-area single-crystal wafers of cubic SiC for semiconductor devices. *Applied Physics Letters* **1983**, *42*, 460–462.
21. Ouerghi, A.; Marangolo, M.; Belkhou, R.; El Moussaoui, S.; Silly, M. G.; Eddrief, M.; Largeau, L.; Portail, M.; Fain, B.; Sirotti, F. Epitaxial graphene on 3C-SiC(111) pseudosubstrate: Structural and electronic properties. *Phys. Rev. B* **2010**, *82*, 125445.
22. Ouerghi, A.; Belkhou, R.; Marangolo, M.; Silly, M.; El Moussaoui, S.; Eddrief, M.; Largeau, L.; Portail, M.; Sirotti, F. Structural coherency of epitaxial graphene on 3C–SiC (111) epilayers on Si (111). *Applied Physics Letters* **2010**, *97*, 161905.
23. Gupta, B.; Di Bernardo, I.; Mondelli, P.; Della Pia, A.; Betti, M.; Iacopi, F.; Mariani, C.;

- Motta, N. Effect of substrate polishing on the growth of graphene on 3C-SiC (111)/Si (111) by high temperature annealing. *Nanotechnology* **2016**, *27*, 185601.
24. Saddow, S. E.; Starke, U.; Coletti, C.; Frewin, C. L.; Riedl, C. A Comprehensive Study of Hydrogen Etching on the Major SiC Polytypes and Crystal Orientations. *Silicon Carbide and Related Materials 2008* **2009**, *615*, 589–592.
25. Saddow, S. E.; Starke, U.; Konuma, M.; Lee, W.; Soubatch, S.; Rao, S. P. Structure and Morphology of 4H-SiC Wafer Surfaces after H₂-Etching. *Silicon Carbide and Related Materials 2004* **2005**, *483*, 761–764.
26. Sandin, A.; Rowe, J. J.; Dougherty, D. B. Improved graphene growth in UHV: Pit-free surfaces by selective Si etching of SiC (0001)-Si with atomic hydrogen. *Surface Science* **2013**, *611*, 25–31.
27. Suemitsu, M.; Jiao, S.; Fukidome, H.; Tateno, Y.; Makabe, I.; Nakabayashi, T. Epitaxial graphene formation on 3C-SiC/Si thin films. *Journal of Physics D: Applied Physics* **2014**, *47*, 094016.
28. Ouerghi, A.; Portail, M.; Kahouli, A.; Travers, L.; Chassagne, T.; Zielinski, M. Epitaxial Graphene Elaborated on 3C-SiC (111)/Si Epilayers. *Materials Science Forum* **2010**, *645*, 585–588.
29. Riedl, C.; Starke, U.; Bernhardt, J.; Franke, M.; Heinz, K. Structural properties of the graphene-SiC (0001) interface as a key for the preparation of homogeneous large-terrace graphene surfaces. *Physical Review B* **2007**, *76*, 245406.
30. Mallet, P.; Varchon, F.; Naud, C.; Magaud, L.; Berger, C.; Veuillen, J.-Y. Electron states of mono-and bilayer graphene on SiC probed by scanning-tunneling microscopy. *Physical Review B* **2007**, *76*, 041403.

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31. Gupta, B.; Notarianni, M.; Mishra, N.; Shafiei, M.; Iacopi, F.; Motta, N. Evolution of epitaxial graphene layers on 3C SiC/Si (1 1 1) as a function of annealing temperature in UHV. *Carbon* **2014**, *68*, 563 – 572.
32. Scardamaglia, M.; Lisi, S.; Lizzit, S.; Baraldi, A.; Larciprete, R.; Mariani, C.; Betti, M. G. Graphene-induced substrate decoupling and ideal doping of a self-assembled iron-phthalocyanine single layer. *The Journal of Physical Chemistry C* **2013**, *117*, 3019–3027.
33. Massimi, L.; Ourdjini, O.; Lafferentz, L.; Koch, M.; Grill, L.; Cavaliere, E.; Gavioli, L.; Cardoso, C.; Prezzi, D.; Molinari, E. *et al.* Surface-assisted reactions toward formation of graphene nanoribbons on Au (110) surface. *The Journal of Physical Chemistry C* **2015**, *119*, 2427–2437.
34. Penueles, J.; Ouerghi, A.; Lucot, D.; David, C.; Gierak, J.; Estrade-Szwarckopf, H.; Andreazza-Vignolle, C. Surface morphology and characterization of thin graphene films on SiC vicinal substrate. *Phys. Rev. B* **2009**, *79*, 033408.
35. Malard, L.; Pimenta, M.; Dresselhaus, G.; Dresselhaus, M. Raman spectroscopy in graphene. *Physics Reports* **2009**, *473*, 51–87.
36. Ferrari, A. C.; Basko, D. M. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nature Nanotechnology* **2013**, *8*, 235–246.
37. Faugeras, C.; Nerrière, A.; Potemski, M.; Mahmood, A.; Dujardin, E.; Berger, C.; De Heer, W. Few-layer graphene on SiC, pyrolytic graphite, and graphene: A Raman scattering study. *Applied Physics Letters* **2008**, *92*, 011914.
38. Nakashima, S.-i.; Harima, H. Raman investigation of SiC polytypes. *Physica Status Solidi (a)* **1997**, *162*, 39–64.

39. Röhrli, J.; Hundhausen, M.; Emtsev, K.; Seyller, T.; Graupner, R.; Ley, L. Raman spectra of epitaxial graphene on SiC (0001). *Applied Physics Letters* **2008**, *92*, 201918.
40. Lee, D. S.; Riedl, C.; Krauss, B.; von Klitzing, K.; Starke, U.; Smet, J. H. Raman spectra of epitaxial graphene on SiC and of epitaxial graphene transferred to SiO₂. *Nano Letters* **2008**, *8*, 4320–4325.
41. Ferralis, N.; Maboudian, R.; Carraro, C. Evidence of structural strain in epitaxial graphene layers on 6H-SiC (0001). *Physical Review Letters* **2008**, *101*, 156801.
42. Graf, D.; Molitor, F.; Ensslin, K.; Stampfer, C.; Jungen, A.; Hierold, C.; Wirtz, L. Spatially resolved Raman spectroscopy of single-and few-layer graphene. *Nano Letters* **2007**, *7*, 238–242.
43. Neumann, C.; Reichardt, S.; Venezuela, P.; Drögeler, M.; Banszerus, L.; Schmitz, M.; Watanabe, K.; Taniguchi, T.; Mauri, F.; Beschoten, B. *et al.* Raman spectroscopy as probe of nanometre-scale strain variations in graphene. *Nature Communications* **2015**, *6*, 8429.
44. Robinson, J. A.; Puls, C. P.; Staley, N. E.; Stitt, J. P.; Fanton, M. A.; Emtsev, K. V.; Seyller, T.; Liu, Y. Raman topography and strain uniformity of large-area epitaxial graphene. *Nano Letters* **2009**, *9*, 964–968.
45. Robinson, J. A.; Wetherington, M.; Tedesco, J. L.; Campbell, P. M.; Weng, X.; Stitt, J.; Fanton, M. A.; Frantz, E.; Snyder, D.; VanMil, B. L. *et al.* Correlating Raman spectral signatures with carrier mobility in epitaxial graphene: a guide to achieving high mobility on the wafer scale. *Nano Letters* **2009**, *9*, 2873–2876.

Supplementary Information: High Quality Epitaxial Graphene by Hydrogen-etching of 3C-SiC(111) thin-film on Si(111)

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XPS analysis on lower temperature annealed samples

Survey XPS data taken on both 3C-SiC(111)-Si H-treated at 1000°C and untreated at 950°C, respectively, are shown in Fig. 1. Data on both samples are very similar as it concerns the O reduction, since a high-temperature annealing of the 3C-SiC(111)-Si sample reduces the natural oxygen contamination present on the as-received surface, even without using H-

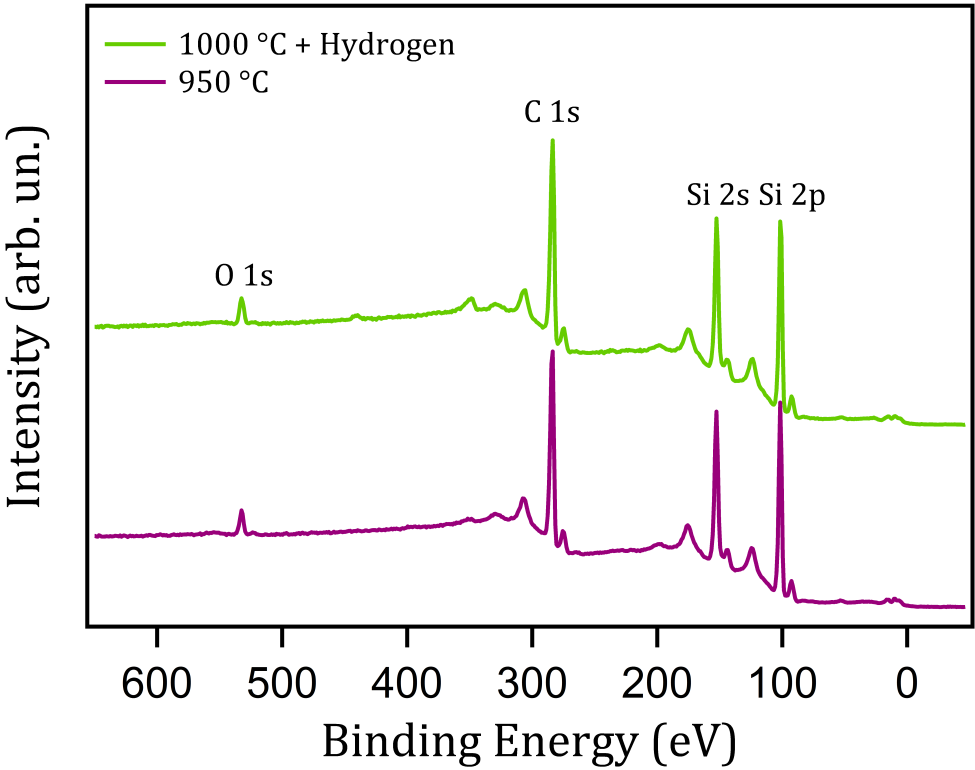


Figure 1: XPS survey data for 3C-SiC(111)/Si(111) after annealing at 1000°C assisted by atomic hydrogen exposure (lower spectrum) and at 950°C without treatment (upper spectrum). Spectra vertically stacked for clarity.

exposure during annealing at lower temperature than that necessary to fully form graphene. In fact, the H-treatment strongly improves the sample surface quality, as outlined in the STM images of the main paper, while the XPS data show an analogous result.

High-resolution C 1s core-level data for both samples (H-treated at 1000°C and untreated at 950°C) are shown in Fig. 2.

Lower temperature annealing than the final T necessary to get full graphene layers, give the same trend observed for 1250°C annealing as it concerns the H-treated and untreated samples. In particular, the G component starts forming above 950°C on both samples. Thus, the atomic hydrogen treatment improves the sample quality already at intermediate temperatures (950-1000°C).

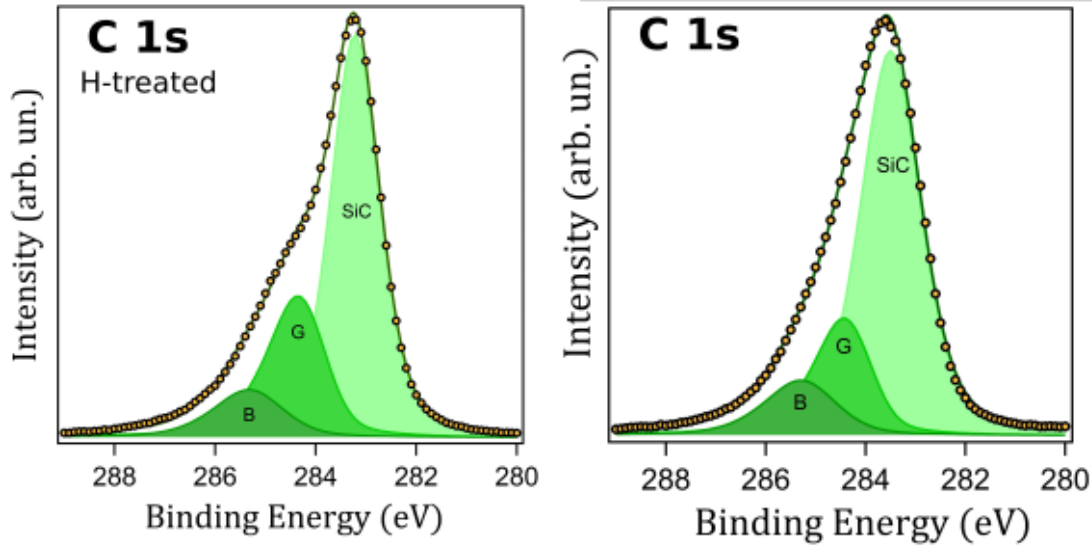


Figure 2: C 1s XPS spectra for intermediate graphene growth on 3C-SiC(111)-Si in UHV at 1000°C with hydrogen-exposure (left) and without H treatment (right). The three different features can be attributed to the substrate (SiC), buffer layer (B) and graphene (G). Experimental data (open dots) and results of the fitting analysis through Voigt curves: sum fitting curve (continuous line), and the three fitting components (coloured peaks).

Raman shift analysis for the untreated substrate

Raman measurements were performed after the final step of the graphene growth without using an hydrogen-etched SiC substrates, to be compared with the Raman data shown in the main paper. All the typical peaks associated with graphene layer/s were fitted with lorentian curves, and along with the contributions coming from the SiC substrate, are plotted in Fig. 3.

Position, band-width and relative intensity of every band in the Raman spectrum (Table 1) are in excellent agreement with those recently presented in literature for a sample grown with the same procedure,¹ and they do not show strong differences compared with the Raman results obtained on the hydrogen-etched sample (shown in the main paper). In fact, the Raman spectra are strongly influenced by the rather large strain,^{2,3} associated to the

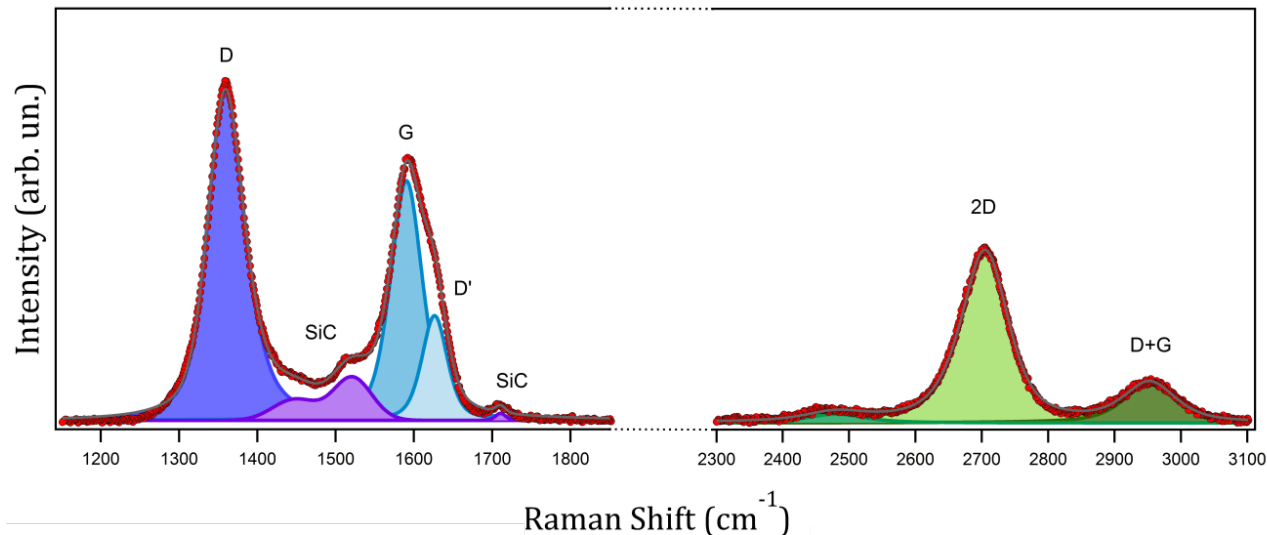


Figure 3: Raman of graphene grown on 3C-SiC/Si(111), without Hydrogen etching. G and 2D bands, typical of graphene, D and D' due to defects, and *SiC* features arising from the substrate. Peak parameters resulting from a fitting analysis with lorentzian curves, is plotted in Table 1.

growth on the underlying SiC substrate, responsible for the G-band blueshift and 2D-band broadening. These data confirm that Raman spectroscopy on graphene for samples affected by important strain effects, cannot be straightly used for determining the number of graphene layers. However, the D' shoulder of the main G band appears higher than in the H-treated sample, bringing to light the presence of more defects in the un-treated sample with respect to the treated one.

Table 1: Fit results of the Raman spectra of the untreated sample.

| | Position (cm^{-1}) | FWHM (cm^{-1}) | Area (arb. un.) |
|----------|------------------------|--------------------|-----------------|
| D band | 1360.2 | 57 | 1559 |
| G band | 1590.4 | 48 | 934 |
| D' band | 1626.4 | 38.4 | 327 |
| 2D band | 2704.0 | 84.9 | 1258 |
| D+G band | 2953.0 | 92.6 | 314 |

References

1. Gupta, B.; Notarianni, M.; Mishra, N.; Shafiei, M.; Iacopi, F.; Motta, N. Evolution of epitaxial graphene layers on 3C SiC/Si (1 1 1) as a function of annealing temperature in UHV. *Carbon* **2014**, *68*, 563 – 572.
2. Lee, D. S.; Riedl, C.; Krauss, B.; von Klitzing, K.; Starke, U.; Smet, J. H. Raman spectra of epitaxial graphene on SiC and of epitaxial graphene transferred to SiO₂. *Nano Letters* **2008**, *8*, 4320–4325.
3. Neumann, C.; Reichardt, S.; Venezuela, P.; Drögeler, M.; Banszerus, L.; Schmitz, M.; Watanabe, K.; Taniguchi, T.; Mauri, F.; Beschoten, B. *et al.* Raman spectroscopy as probe of nanometre-scale strain variations in graphene. *Nature Communications* **2015**, *6*, 8429.