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Improving the graphene quality for the integration in silicon-based semiconductor devices

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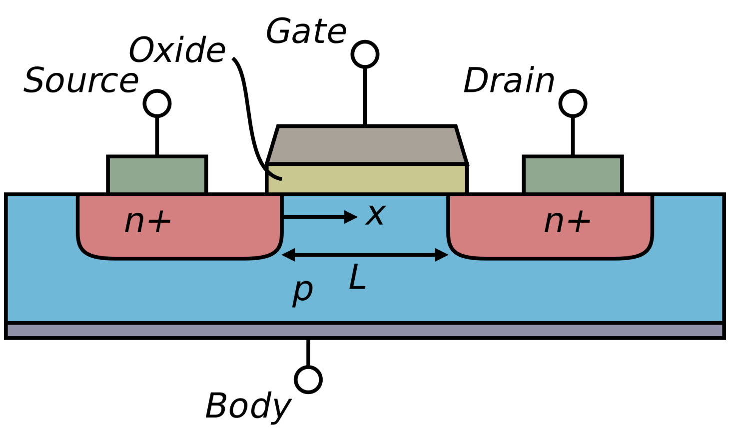
Graphene Properties

Graphene is a very promising material in a wide range of engineering field: mechanics, optoelectronics and electronics.

- Specific surface area 2600 m^2/g
- Yield stress 130 GPa
- Thermal conductivity 5300 W/m·K

- Absorbance 2,3 %
- Transmittance 97,7 %
- **Carrier mobility $2\cdot10^5$ cm^2 /V·s (100 times better than silicon)**

Graphene integration in a MOSFET would imply:

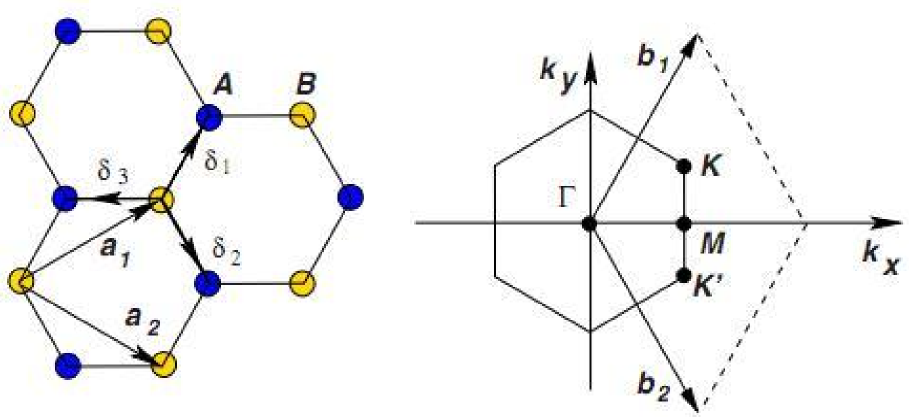


1) Reducing the dimensions of the device

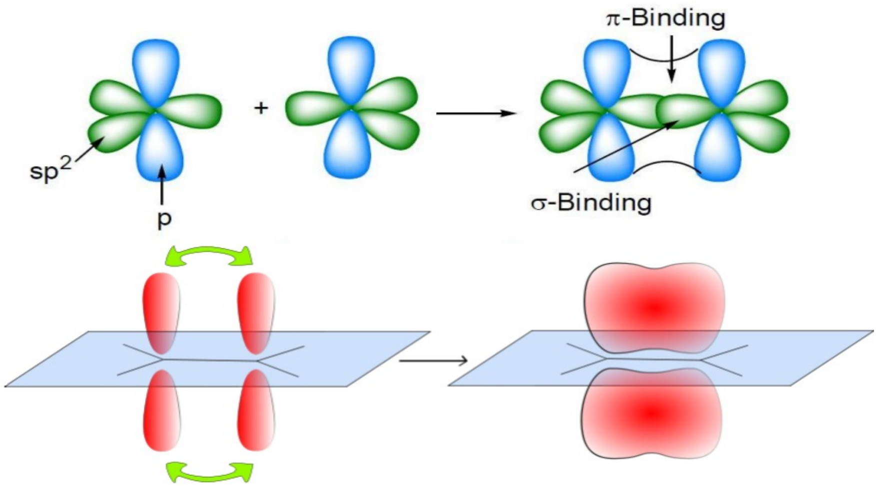
2) Improving the signal trasfer efficiency in the connections

Graphene Properties

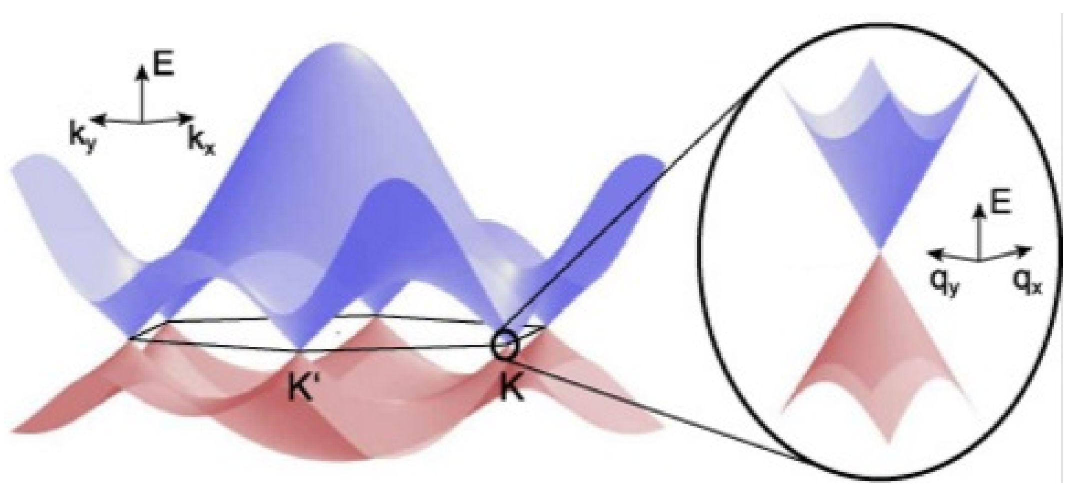
Direct and reciprocal lattice



Sp_2 hybridization

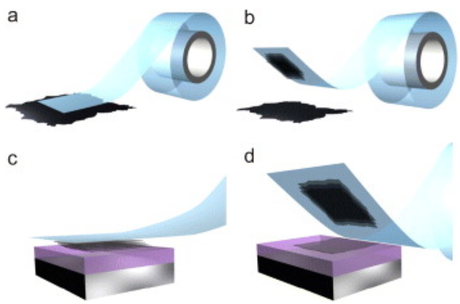


π and π' bands formation

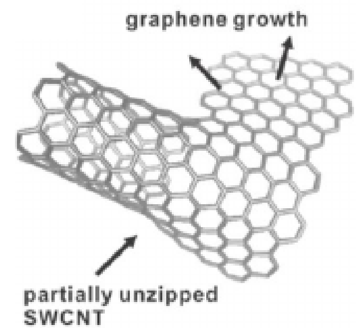


Graphene Synthesis

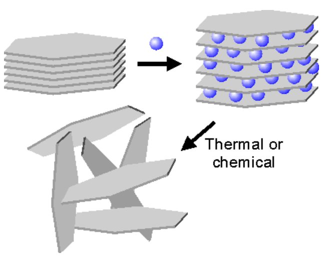
Mechanical cleavage



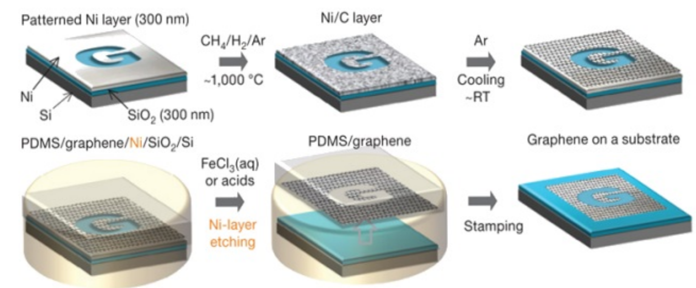
CNTs unzipping



Chemical exfoliation

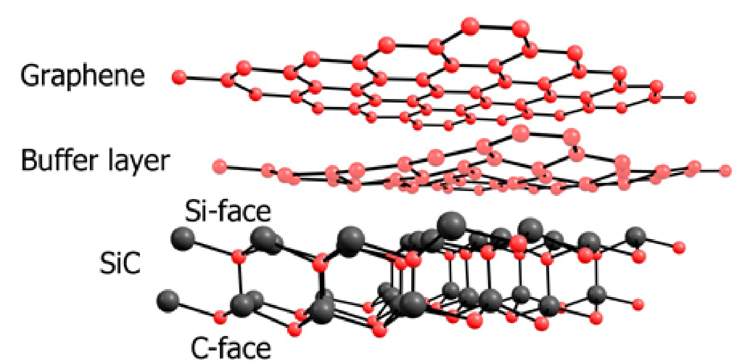


CVD



- Limited control over dimensions
- Further purification is needed
- Transfer to desired substrate
- No mass production process
- High production costs

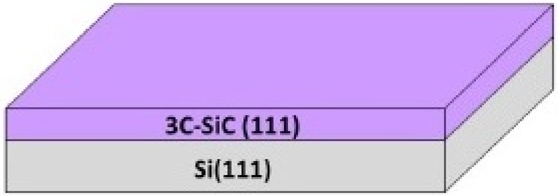
Thin-Film SiC graphitization in UHV



K.S. Novoselov et al. Nature 490 (2012)

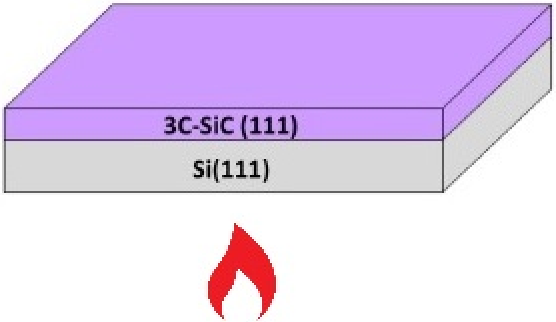
SiC Graphitization

Graphitization of a thin-film 3C-SiC\Si in UHV



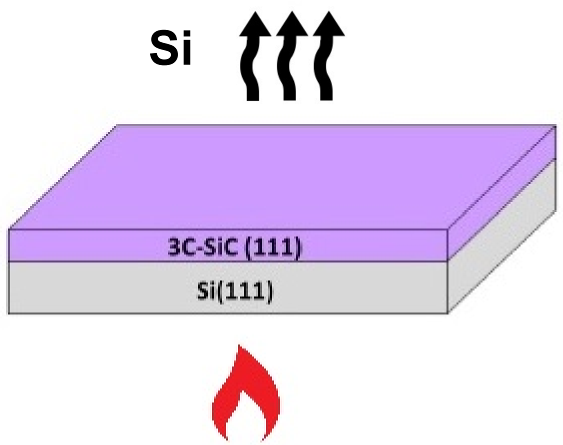
SiC Graphitization

Graphitization of a thin-film 3C-SiC\Si in UHV
T~950 °C for 10 min



SiC Graphitization

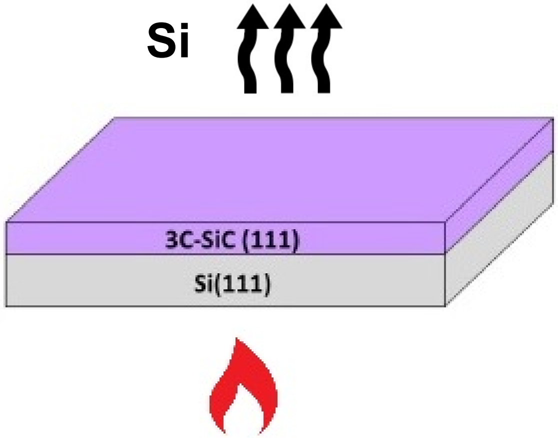
Graphitization of a thin-film 3C-SiC\Si in UHV
T~950 °C for 10 min; T~1250°C for 10 min

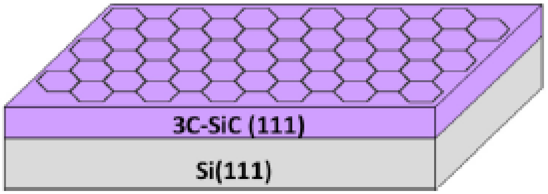


SiC Graphitization

Graphitization of a thin-film 3C-SiC\Si in UHV

T~950 °C for 10 min; T~1250°C for 10 min





Buffer layer formation

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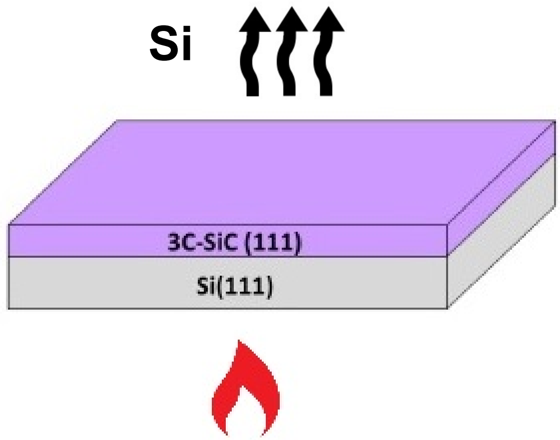
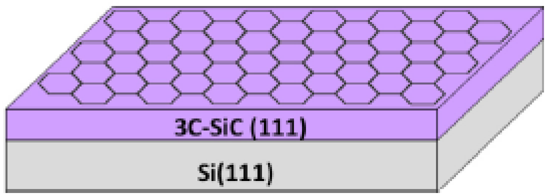
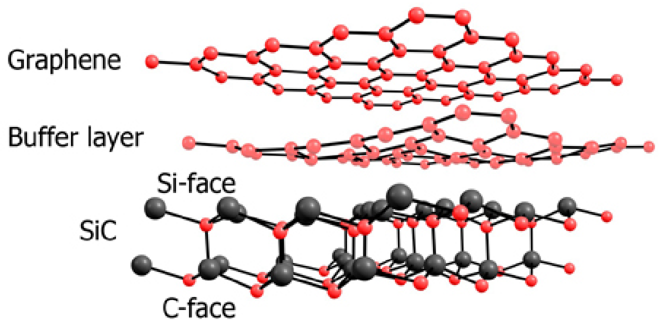




Buffer layer formation



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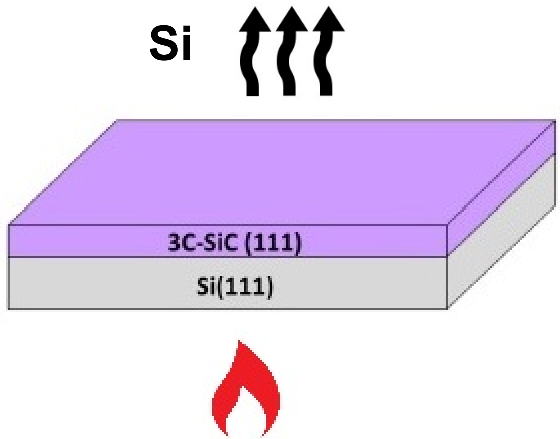
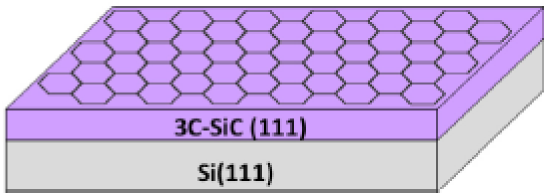
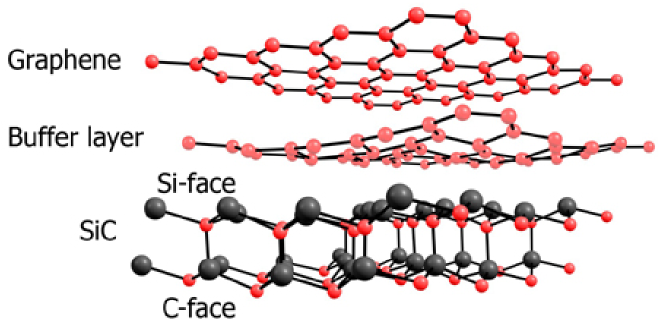




Buffer layer formation



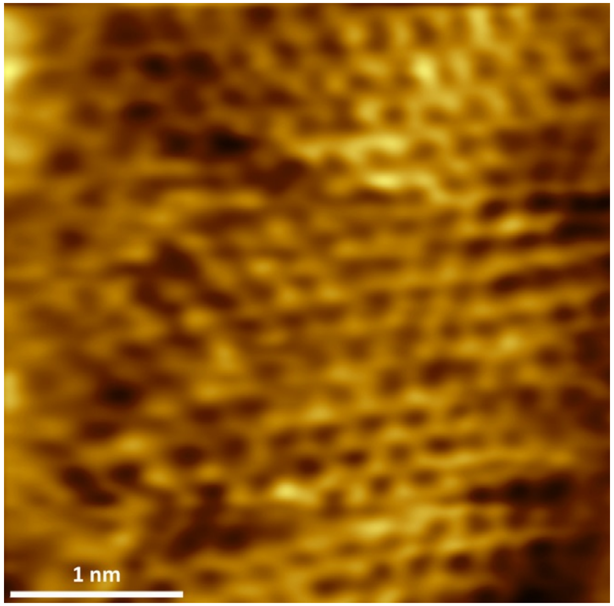
Property	4H-SiC	6H-SiC	3C-SiC	Si
Thermal conductivity (W/cm-K)	4.9	4.9	3.2	1.5
Lattice constant (a, c in Å)	a=3.0730	a=3.0806	a=4.3596	a=5.43095

The cubic politype is the only one compatible with Si lattice

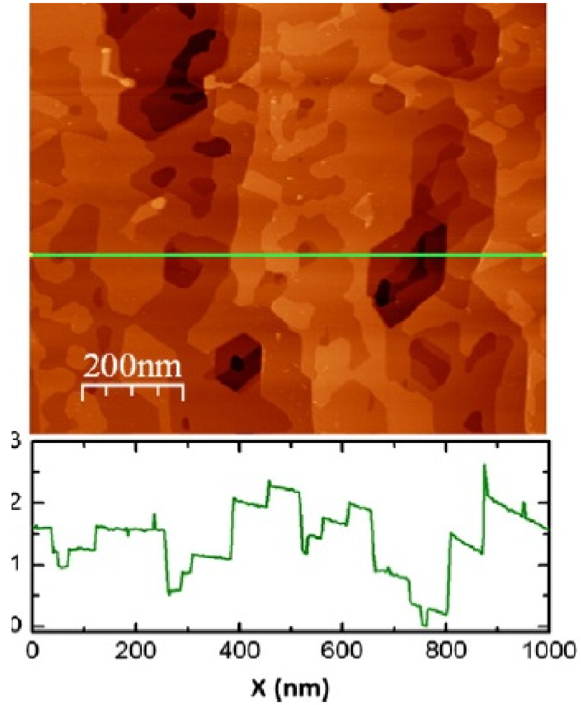
B.Gupta et al. Carbon 68 (2014)

Graphitization Issues

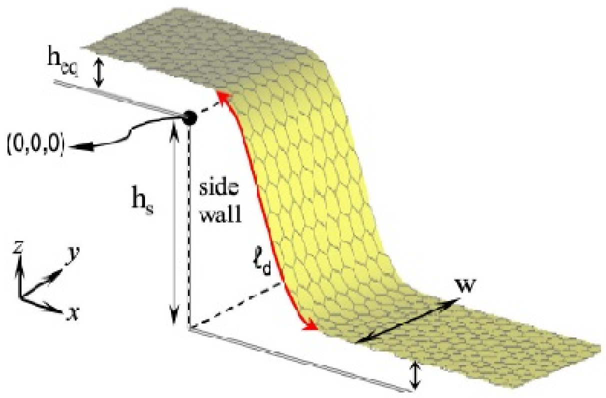
Lattice defects

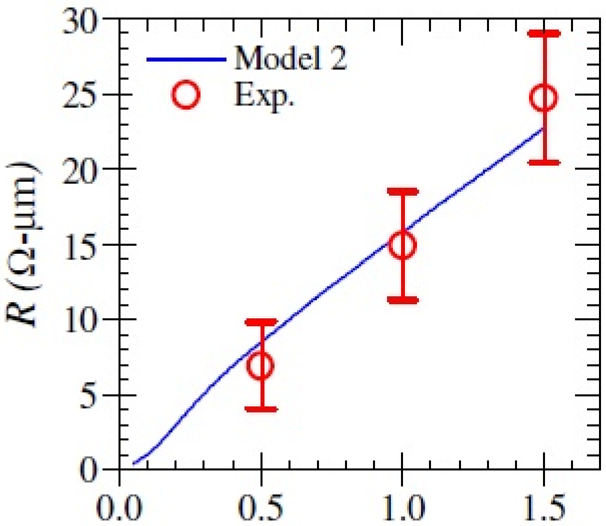


Pits and steps



Resistivity dependence





Improvements with:

Graphitization in Ar Atmosphere at 2000° C

- Melting point of silicon is 1400° C
- Unfeasibile integration

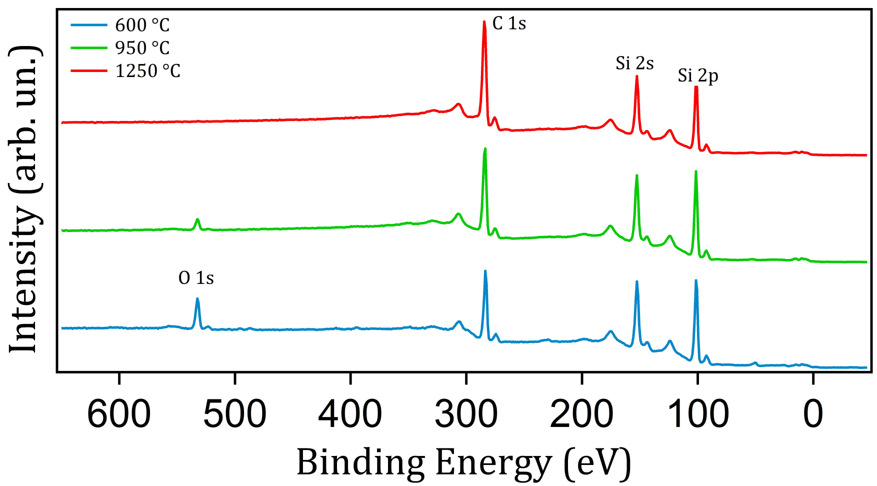
→ Graphitization of 3C-SiC thin-film **polished** in UHV

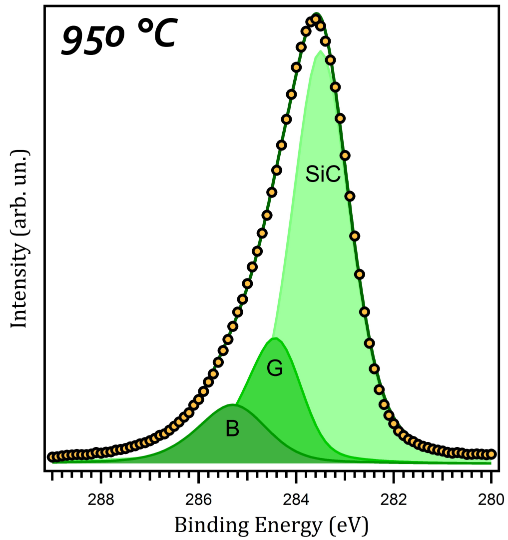
→ Monoatomic **hydrogen etching** of polished 3C-SiC thin-film

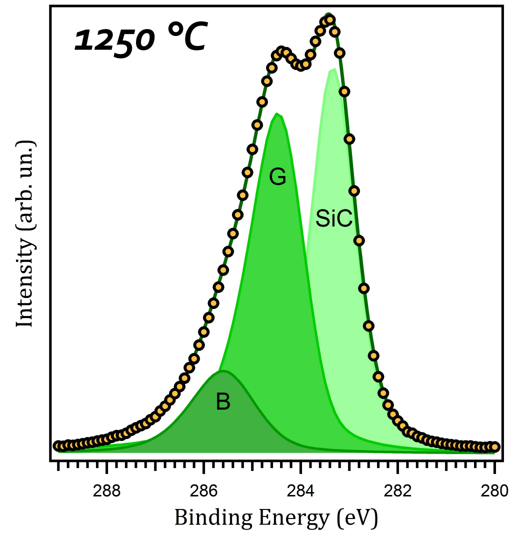
Forti, S., et al. Physical Review B 84.12 (2011): 125449;B.Gupta et al. Carbon 68 (2014); A. Sandin et al. Surf. Sci 611 (2013)

XPS: C1s Core Level Analysis

Full UHV growth process on CMP samples





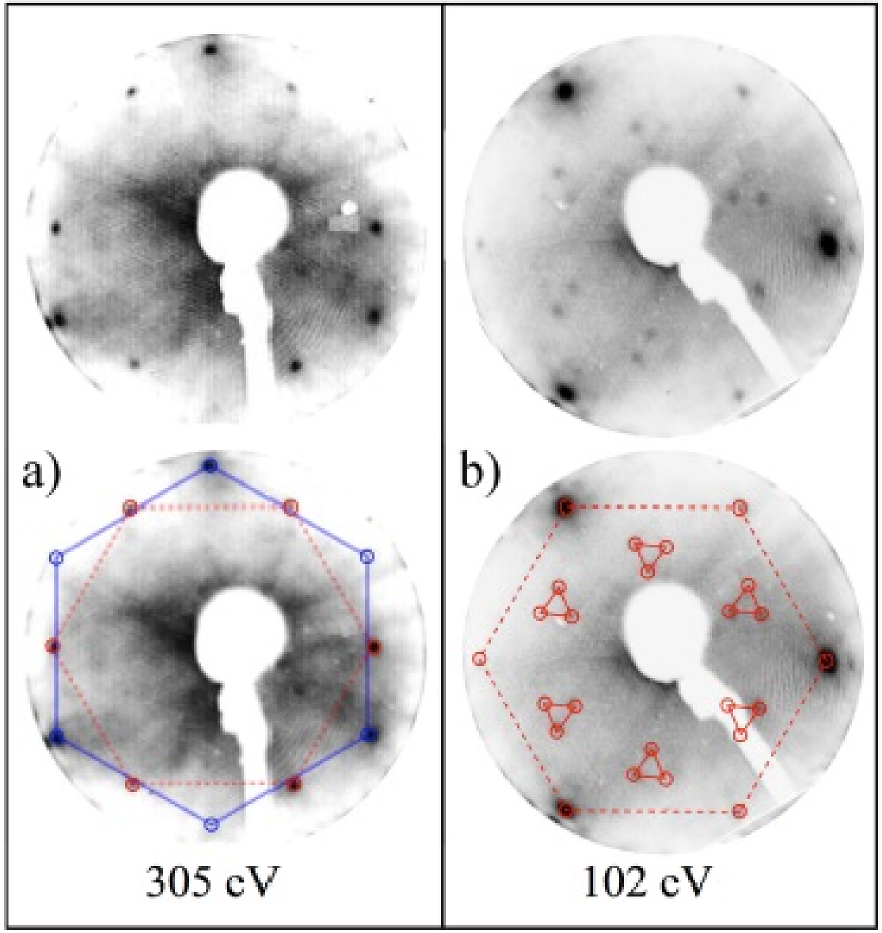


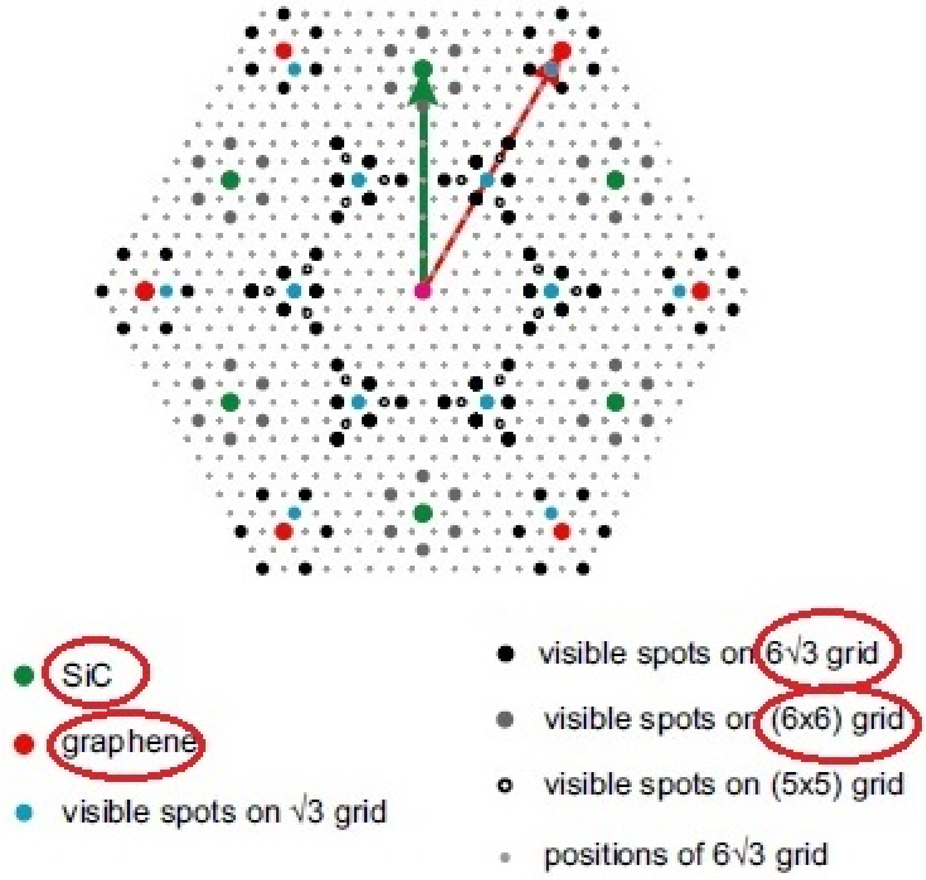
	Position (eV)	FWHM (eV)	Asym.	Area (%)
SiC	283.3 ± 0.5	1.1 eV	0.00	43
G	284.4 ± 0.5	1.5 eV	0.15	44
B	285.6 ± 0.5	1.6 eV	0.06	13

- Energy position of every peak are in good agreement with previous experiments performed on the similar substrates [1][2]
- The asymmetric character of the peaks related to both graphene and buffer layer can be attributed to its conductive/semi-conductive nature [3]
- Through the attenuation of the signal intensity arising from the SiC, it is possible to extimate the number of layers: **~2.8**

LEED Pattern

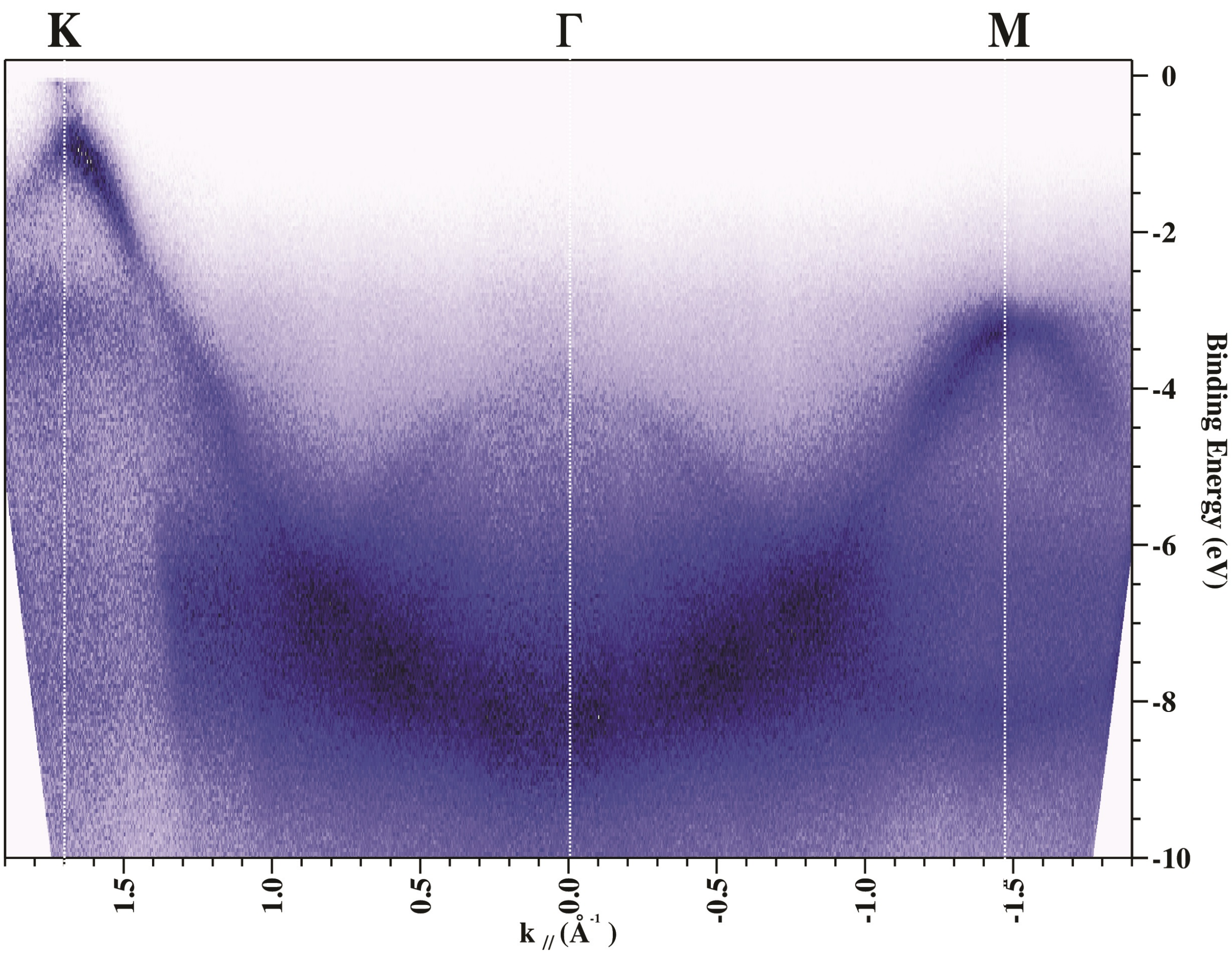
Long-range order of both SiC and Graphene domains





ARPES Spectrum

Valence band acquired at T = 77 K

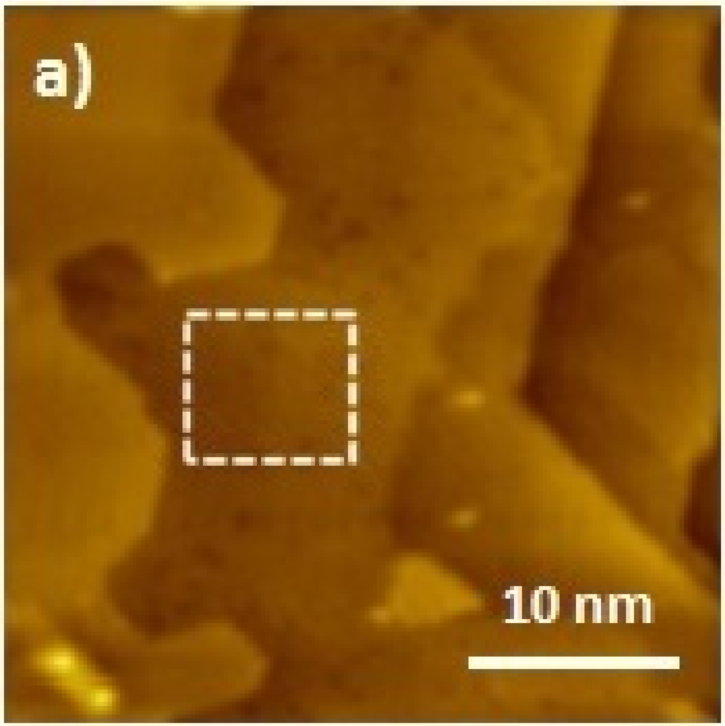


- Typical π band
- Linear dispersion
- E_F shift of 290 mV

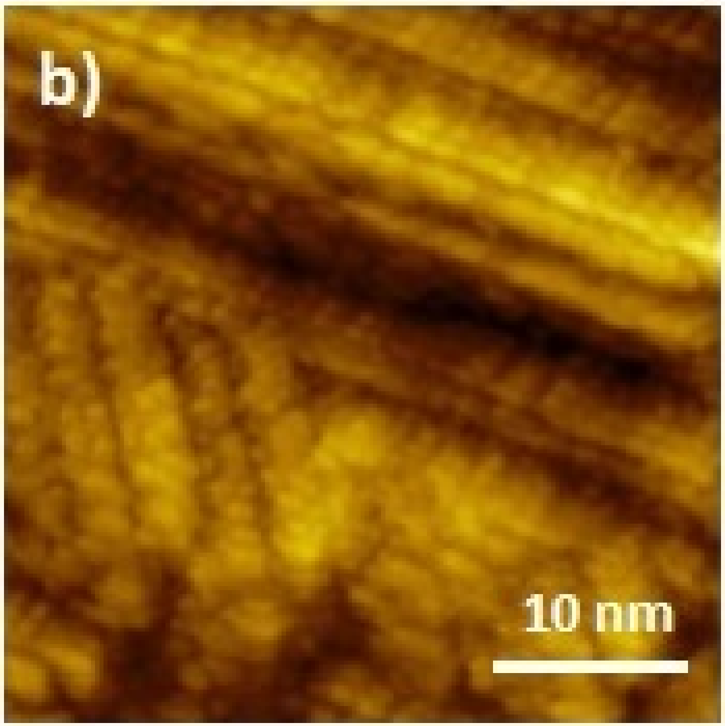
B. Gupta, I. di Bernardo, P. Mondelli et al. Nanotechnology 27 vol 18 (2016)

STM Images

Polished



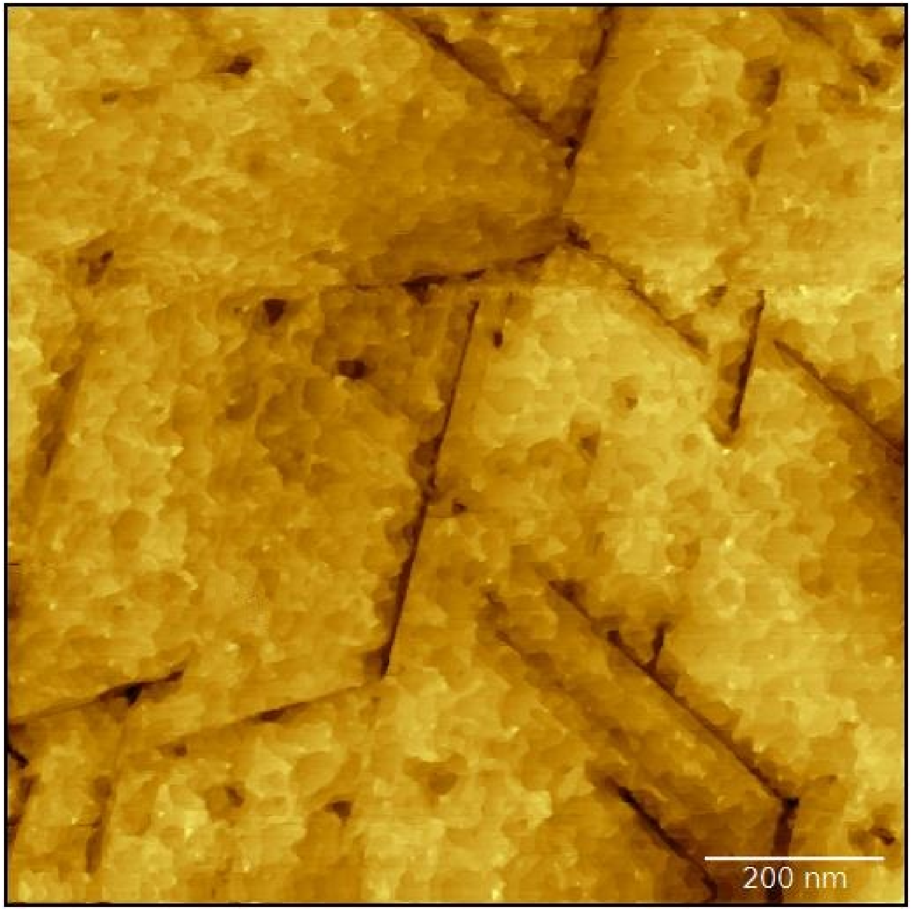
Un-polished

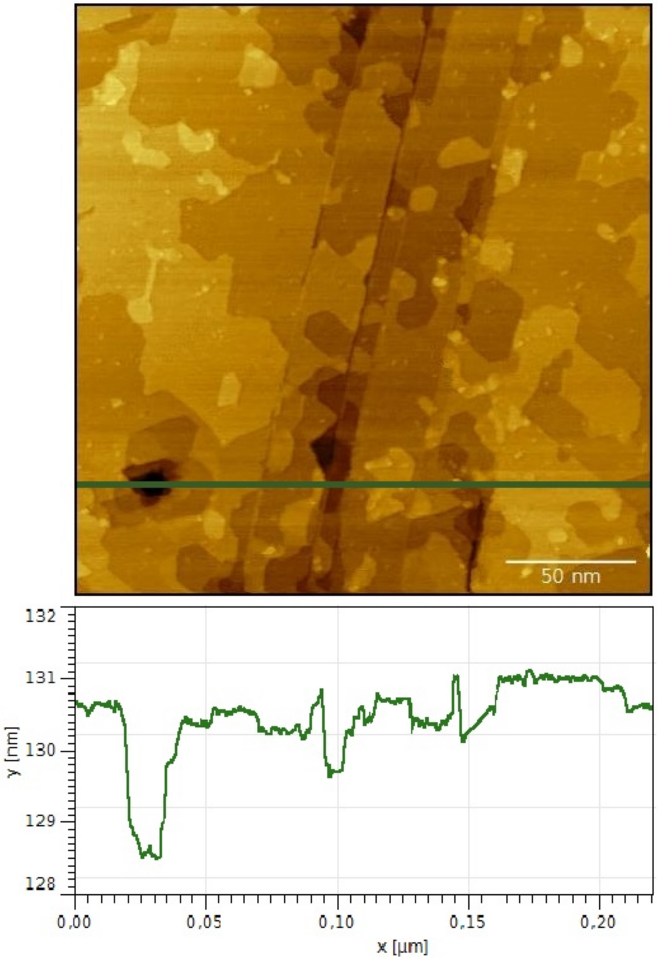


- Graphene's domains on CMP samples are wider

B. Gupta, I. di Bernardo, P. Mondelli et al. Nanotechnology 27 vol 18 (2016)

STM Images

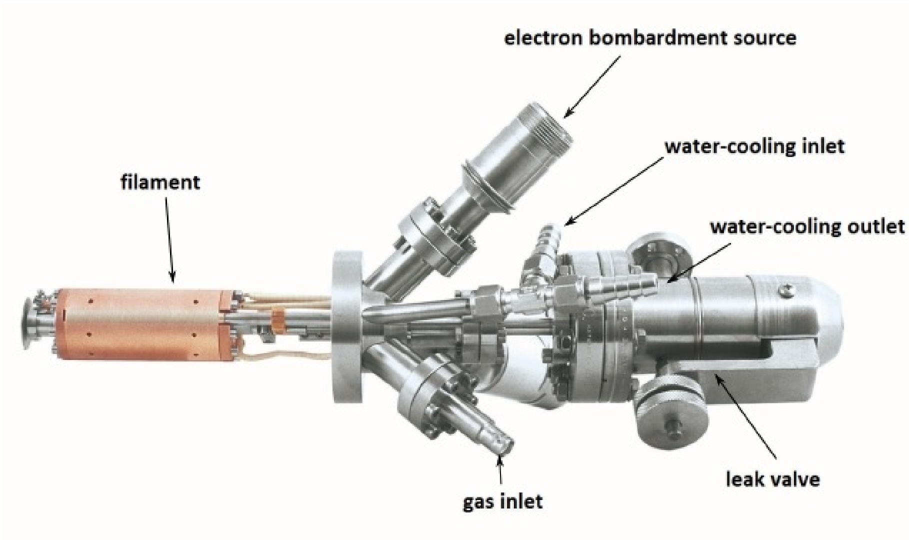




- Significant step-growth
- SiC bilayer width is 2.5 Å, step height up to 4 SiC bilayers
- Pits are still present
- Pits up to ~2 nm thick

Monoatomic H-etching of 3C-SiC CMP

EFM-H Omicron Evaporator



The evaporator provides the required energy in order to ionize an H_2 gas passing through the hot filament. Hydrogen atoms reacts more easily with the Si ones on the substrate surface, leading to a better nucleation of the buffer layer

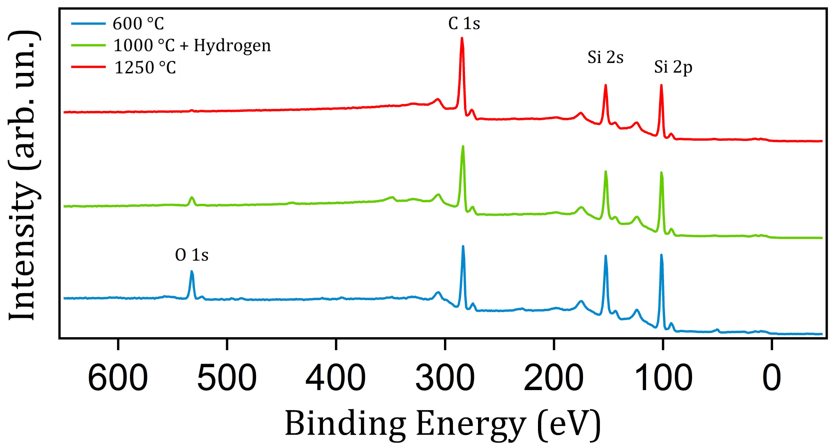
I. Sample cleaning procedure

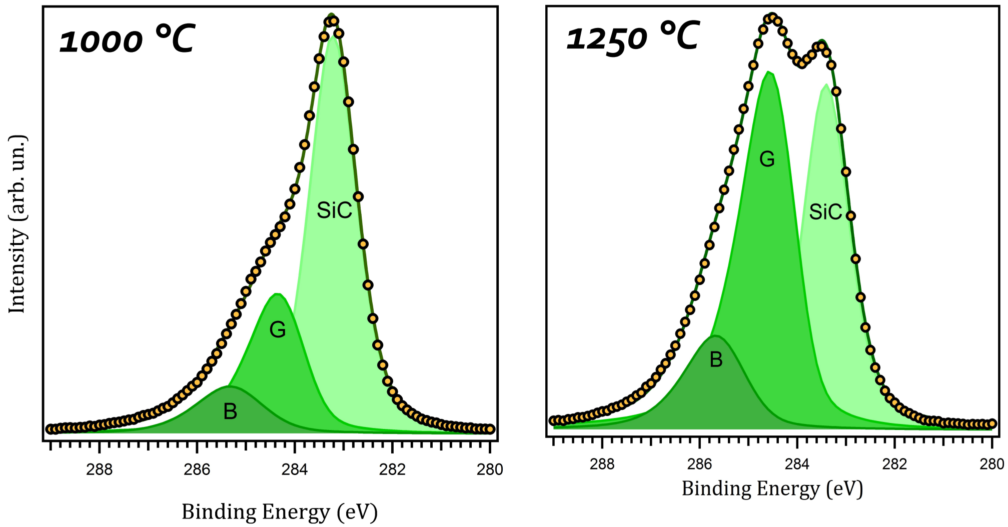
II. Monoatomic hydrogen etching at 1000° C, $P = 7.5 \cdot 10^{-6}$ mbar

III. Annealing for 10 minutes at 1250° C

XPS: C1s Core Level Analysis

Hydrogenated graphene



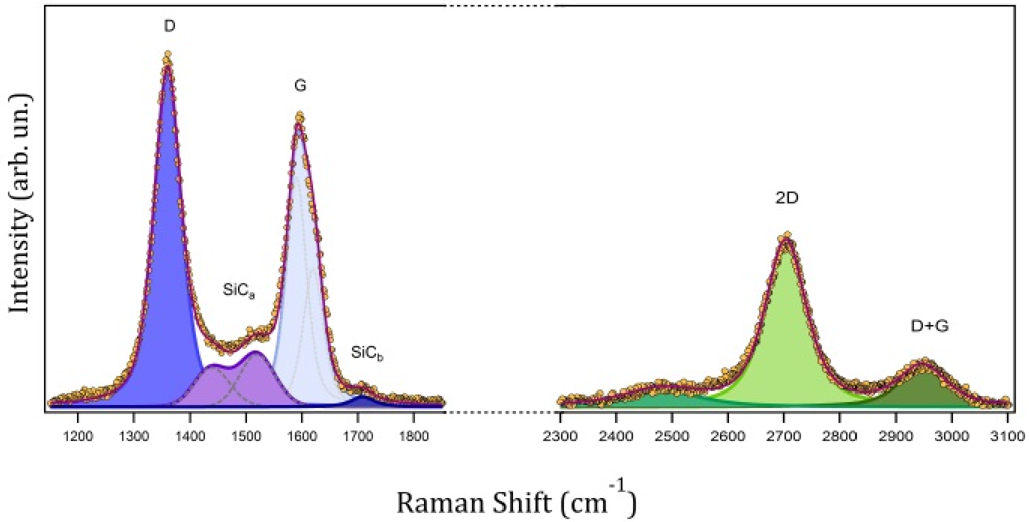


	Position (eV)	FWHM (eV)	Asym.	Area (%)
SiC	283.4 ± 0.5	1.1 eV	0.00	38
G	284.6 ± 0.5	1.5 eV	0.2	48
B	285.7 ± 0.5	1.6 eV	0.1	14

- Lineshape and energy position of each peak are similar to those observed for the full UHV process on CMP samples.
- Through the attenuation of the signal intensity arising from the SiC, it is possible to extimate the number of layers: **~3.2**

B.Gupta et al. Carbon 68 (2014) ; A. Ouerghi et al. App. Phys. Lett 96 191910 (2010); D. Pacilè et al. PRB 90, 195446 (2014)

Raman Shift Analysis



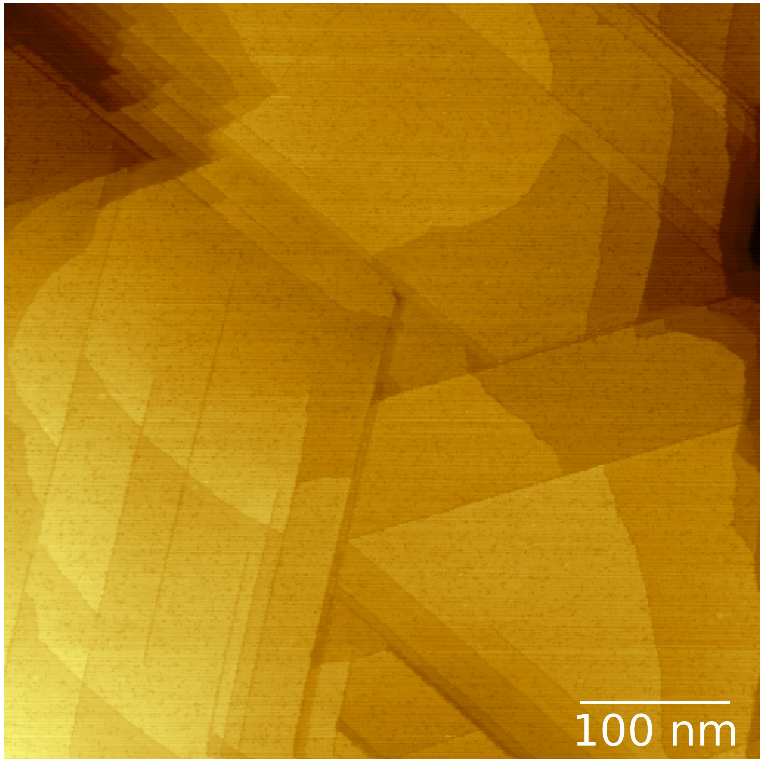
Band	Position (cm-1)	FWHM (cm-1)	Area (Arb. Un)
D	1359.3	55.9	4242
G	1594.4	66.7	3426
2D	2703.4	88.0	3422
D+G	2946.8	100.0	871

- The position of the G-band, blueshifted as compared to micromechanically-cleaved graphene, is in very good agreement with previous experiments performed on SiC substrates [2-4].
- The 2D-band width is heavily influenced by defects and strain induced by the substrate [5-6]
- The present Raman spectrum on graphene/thin-film 3C-SiC on Si, confirms the formation of good quality graphene, comparable to that achieved on bulk SiC[1]

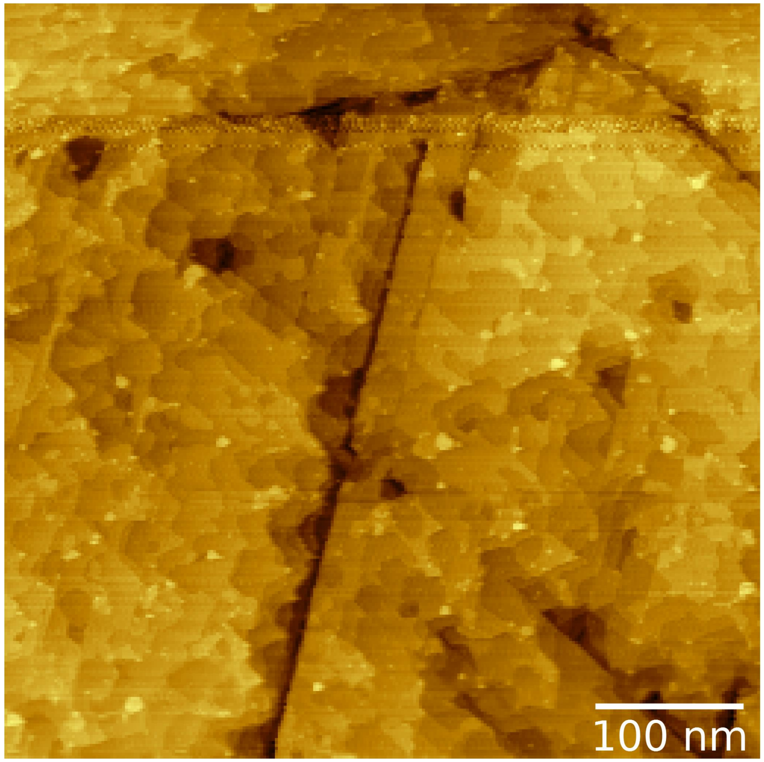
Nano letters 2008, 8, 4320-4325; App. Phys. Lett. 2008, 92, 201918; Phys. Rev. Lett. 2008, 101, 156801; Nano letters 2009, 9, 964-968; Nano letters 2009, 9, 2873-2876

STM Images

Hydrogenated



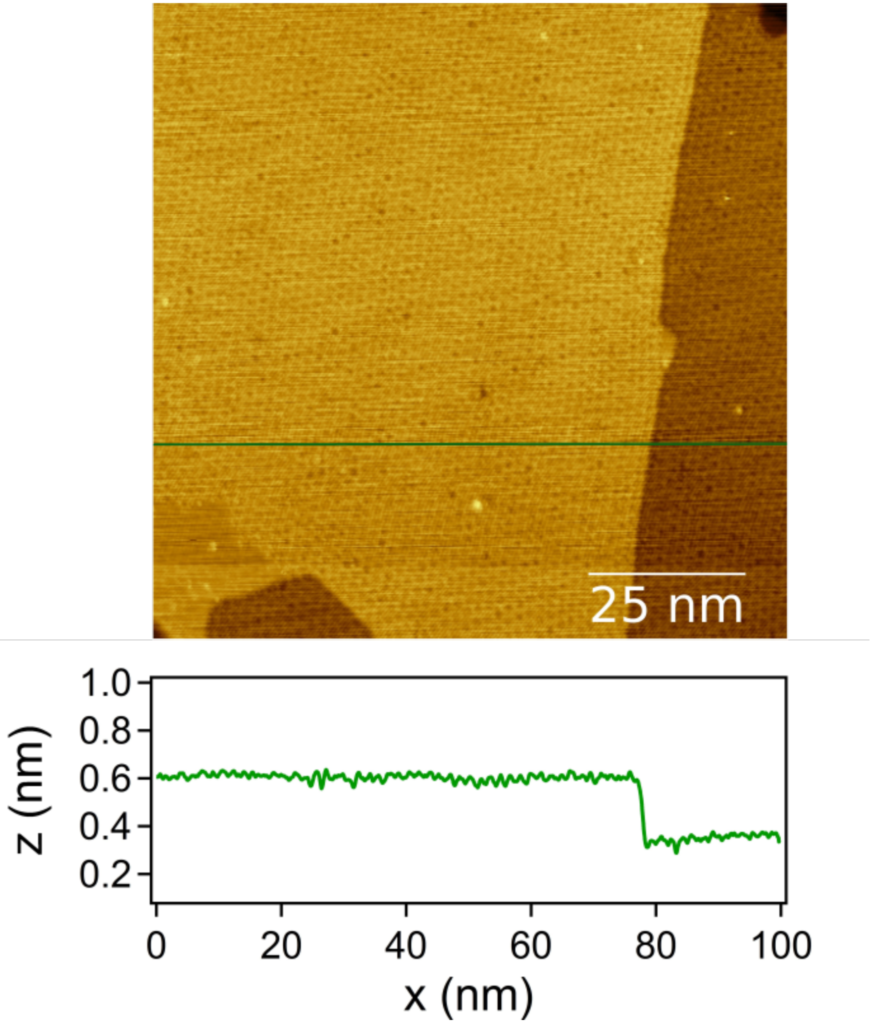
Un-treated



- Domains ~10 times broader
- Complete suppression of pit-formation process

STM Images

Hydrogenated



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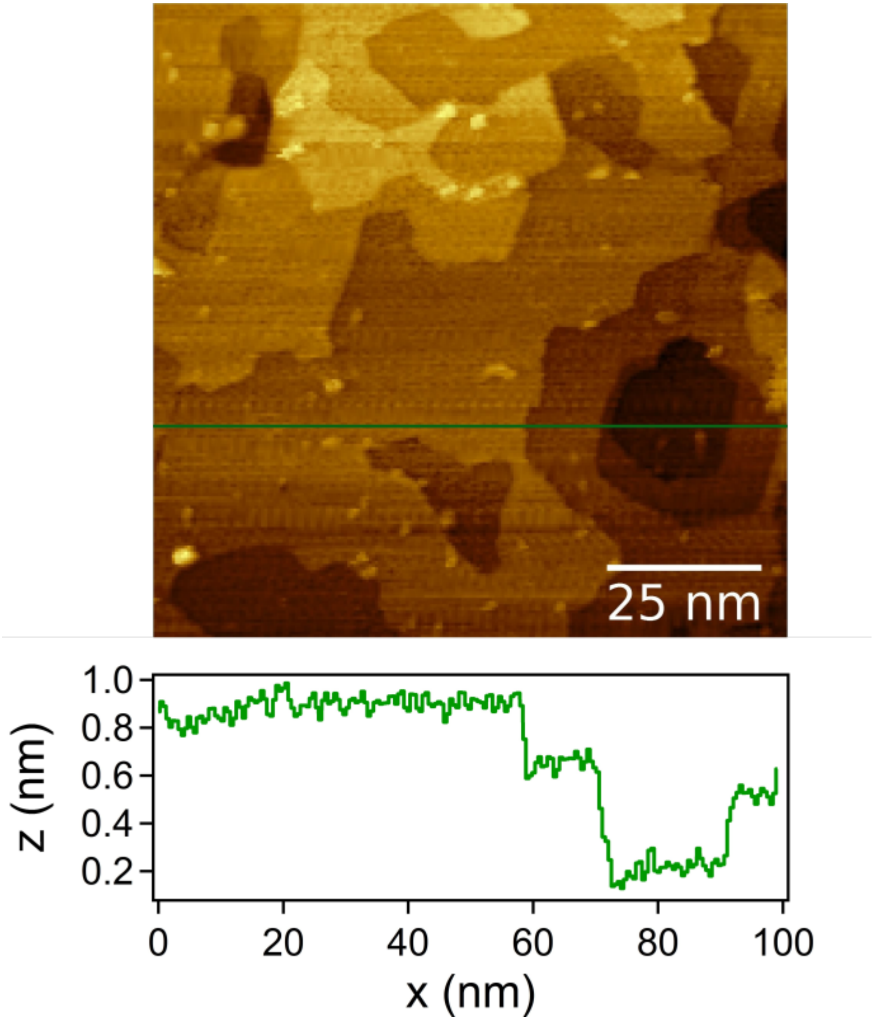

- **Minimum step height for SiC substrates (2.5Å)**

Conclusions

- Identification of a graphene growth process (UHV SiC graphitization) compatible with industrial relevant substrates (silicon-based)
- Performing it using **thin-film polished sample** it was found that:
  - ✔ Electronic and structural properties typical of graphene
  - ✔ No clusters observed
  - ✔ Broader domain dimension
  - ✘ Pits and high density of steps are still detected
- Introduction of a pristine step performed in monoatomic hydrogen atmosphere (**hydrogen etching**) so that:
  - ✔ No pit detected
  - ✔ Increasing the domain dimension by a factor of 10
  - ✔ Remarkable reduction of the step height

All of these results are a step towards the recovery of the free-standing graphene properties on a bottom-up process

Acknowledgements

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- Prof. Nunzio Motta