Growth of homogenous large area graphene on SiC crystals and Cu foil

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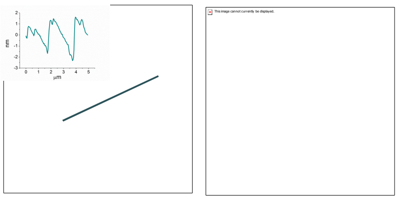
Abstract: In this work homogenous large area graphene is obtained on the silicon and on the carbon face of hexagonal SiC crystals via thermal decomposition and on Cu foil via chemical vapor deposition (CVD). Structural, chemical and electronic properties are characterized by using atomic force microscopy (AFM), scanning electron microscopy (SEM), Raman spectroscopy, and scanning tunnelling microscopy. On SiC graphene is homogenous in thickness within areas ranging from tens to hundreds of microns. On Cu we obtain single crystal domains with lateral dimensions of hundreds of microns.

Hexagonal SiC crystals

Epitaxial Graphene on Si-face

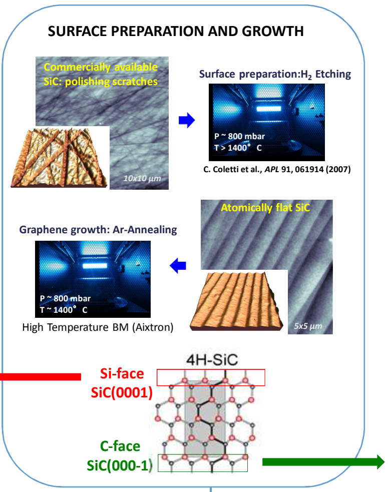
- Buffer layer of C atoms arranged in a honeycomb structure and covalently bound to Si atoms.
- Better graphene thickness control and uniformity.
- Defined azimuthal orientation with respect to the substrate.
- Ordered stacking of layers.
- **In this work we analyze mono – bilayer graphene on SiC(0001).**

ATOMIC FORCE MICROSCOPY (AFM)



Topography and phase AFM images showing graphene monolayer (lighter contrast) and bilayer (darker contrast) domains.

SURFACE PREPARATION AND GROWTH

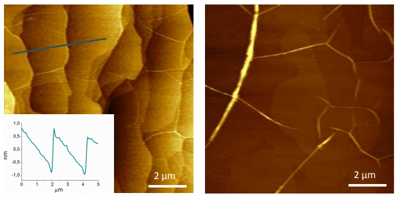


C. Coletti et al., *APL* 91, 061914 (2007)

Epitaxial Graphene on C-face

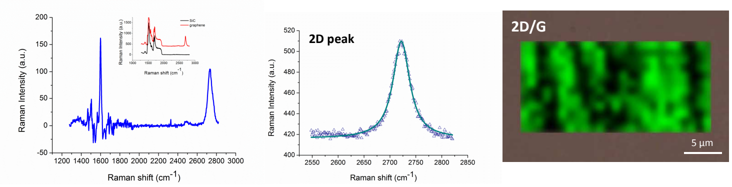
- Difficult control of the number of layers during growth.
- Different azimuthal orientations (turbostratic graphene).
- Electronically decoupled graphene layers .
- Higher mobilities.
- **In this work we analyze ca. 5 layer graphene on SiC(000-1).**

ATOMIC FORCE MICROSCOPY (AFM)



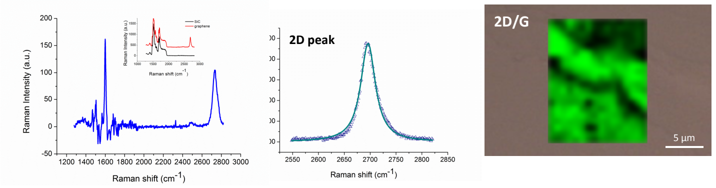
Topography and phase AFM images of two different regions, showing domains separated by narrow ridges (2-3 nm high) and step bunching.

RAMAN SPECTROSCOPY



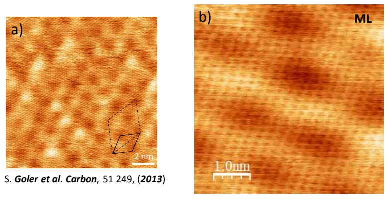
- Raman spectra measured at 532 nm, after subtraction of SiC background, show G peak at ~1590 cm^{-1} and 2D peak at ~2700 cm^{-1}.
- 2D peak fit with one Lorentzian, FWHM 39 cm^{-1}.
- 2D/G map shows a high ratio between 0.7 and 1.2 with low values at the terrace edges.

RAMAN SPECTROSCOPY



- Raman spectra measured at 532 nm, after the subtraction of SiC background, show G peak at ~1590 cm^{-1} and 2D peak at ~2700 cm^{-1}.
- 2D peak fit with one Lorentzian, FWHM 34 cm^{-1}.
- 2D/G map shows a high ratio between 0.7 and 2.5 with low values at the terrace edges.

SCANNING TUNNELLING MICROSCOPY (STM)

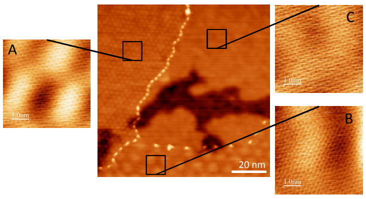


S. *Goler et al. Carbon,* 51 249, (*2013*)

a) A typical STM image obtained while measuring ML graphene reveals the (6√3x6√3)R30° and (6x6) superstructures which are indicated by the dashed and the solid diamond, respectively.

b) The honeycomb lattice signature of graphene is visible on top of the long range superstructure which is due to the interaction of the buffer layer with the substrate.

SCANNING TUNNELLING MICROSCOPY (STM)



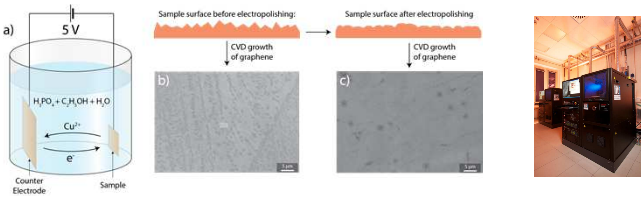
Because on the C face the buffer layer is absent, rotational disorder arises.

The Moiré patterns visible in (A) and (B) are due to misorientation bewteen the two outermost layers. The periodicity *D* of the pattern is given by *D=a/[2 sin(ϑ/2)]*, where *a* is the lattice parameter and *ϑ* is the misorientation angle between the layers. From the measured values of *D* we derive ϑ_A= 4.8° and ϑ_B= 1.6° .

The area (C) probably corresponds to a Bernal stacking or to small periodicities difficult to resolve.

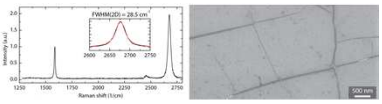
Cu foil

SUBSTRATE PREPARATION: ELECTROCHEMICAL POLISHING OF Cu FOR LARGE GRAIN GRAPHENE GROWTH

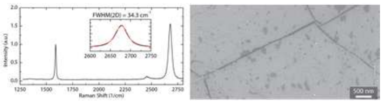


- Cu pre-treatment is crucial in order to improve the quality of the grown graphene.
- Electrochemical polishing cleans the foil and reduces surface roughness which leads to lower nucleation density and in consequence larger grain size.
- SEM images (b) and (c) compare the graphene grown on untreated and electropolished foil, respectively. Notably, the electropolished sample shows only a few bilayer grains which suggest much sparser nucleation and larger crystals (as confirmed by TEM analysis).
- Graphene grown using methane (CH_4) in an Aixtron Black Magic 4-inch cold wall CVD reactor.

THE EFFECT OF Cu ETCHING ON THE QUALITY OF THE TRANSFERRED GRAPHENE



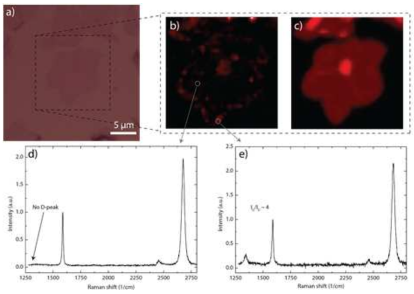
a) **Ammonium persulfate, $(NH_4)S_2O_8$** – Puriss, ACS, >98% (Sigma-Aldrich)



b) **Iron (III) chloride hexahydrate, $FeCl_3 \cdot 6H_2O$** – Puriss, ACS, 98-102% (Sigma-Aldrich)

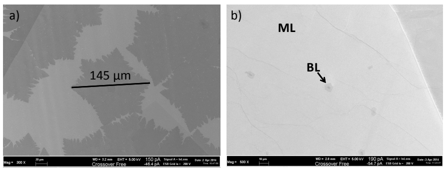
- Cu is a poor substrate for most applications and is etched away to transfer graphene to other substrates.
- The choice of the etchant has a strong impact on the quality of the transferred graphene.
- Samples transferred using ammonium persulfate (a) appear clean in SEM images and have no D-peak and narrow 2D (ca. 29 cm^{-1})
- Samples transferred using iron chloride (b) have a detectable D peak, higher chemical contamination (as confirmed by TEM) and the 2D peak is generally broader.

PARTIAL COVERAGE SAMPLE FOR ACCURATE RAMAN ANALYSIS



- The appearance of Raman D-peak is often caused by grain boundaries, making it difficult to assess the growth and transfer quality of samples with full graphene coverage.
- Partial coverage samples can be useful to determine grain size and to ensure accurate Raman analysis.
- (a) optical image of a single grain of CVD graphene.
- (b) and (c): Raman maps of integrated intensity of D-peak and 2D-peak, respectively.
- (d) and (e): Raman spectra taken from inside a grain and an edge, respectively.

OBTAINING LARGE AREA SINGLE CRYSTALS GRAPHENE GRAINS



- By reducing methane flow and confining the sample is possible to further reduce the density of nucleation centers.
- In this way single crystal graphene grains with lateral dimensions ranging between 100 and 200 microns can be obtained.
- SEM images (a) and (b) show partial and complete coverage growth of graphene on Cu. The lateral dimension of the single crystal grain is also confirmed by TEM analysis.