# Scalable control of graphene growth on 4H-SiC C-face using decomposing silicon nitride masks. [1,2]

**Renaud Puybaret**[1,2]**,** John Hankinson[3], James Palmer[3], Abdallah Ougazzaden[1,2], Paul L Voss[1,2], Claire Berger[3,4] and Walt A de Heer[3]

[1]Georgia Tech Lorraine, GT-CNRS UMI 2958, 57070 Metz, France
[2]Georgia Institute of Technology, School of ECE, Atlanta, GA 30332
[3]Georgia Institute of Technology, School of Physics, Atlanta, GA 30332
[4]CNRS / Institut Néel, BP166, 38042 Grenoble, France

rpuybaret3@mail.gatech.edu

**Abstract**
Epitaxial graphene on silicon carbide (SiC) has great potential for electronics [3-6] with unique physical attributes leading to half-eV band-gap structures [7], exceptional ballistic transport in sidewall nanoribbons [8] or also high-frequency transistors [9,10] and even highly efficient spintronics [11]. Because SiC is a monocrystalline semiconducting industrial substrate, epitaxial graphene on SiC is directly compatible with established scalable device fabrication techniques, making it attractive for advanced electronic devices [5,12]. Patterning of graphene devices is a key step in the fabrication process. In most cases, 2D graphene is first grown then patterned by oxygen plasma. Selective area growth (SAG) is a more straightforward approach, as it provides shaped structures in a single-step process, during epitaxy itself, without requiring the usual post-growth lithography-and-etching steps. Several techniques have been reported for selective area growth of graphene. These include AlN capping [13], ion implantation of Au or Si [14], and sidewall nanoribbons [15].

We report a method for controlling graphene growth down to the sub-micron level, cf Figure 1. We find that deposition of a 120 nm- to 150 nm-thick silicon nitride (SiN) mask on C-face (000-1) silicon carbide prior to graphitization modifies the relative number of multi-layer epitaxial graphene (MEG) sheets. After preparation of the surface of 4H-SiC wafer dies by a high temperature hydrogen etch [16], low-power plasma-enhanced chemical vapor deposition is used for SiN. We have confirmed by AFM measurements after removing SiN with hydrofluoric acid (HF) that the plasma does not result in detectable damage to the SiC surface. Then the sample is graphitized using confinement-controlled sublimation (CCS) [16]. The silicon nitride mask decomposes and vanishes before graphitization is complete. Interestingly, the stoichiometry of the silicon nitride layers controls whether the silicon nitride layer enhances or suppresses graphene growth relative to uncovered areas. We find that N-rich silicon nitride masks decrease the number of layers by three compared to uncovered regions while Si-rich silicon nitride masks increase thickness by two to four layers. The graphene layers of samples prepared with nearly stoichiometric silicon nitride show good mobilities, cf Figure 2, up to 7100 $cm^2.V^{-1}.s^{-1}$, with electron concentrations in the $10^{12}$ $cm^{-2}$ range. Raman spectroscopy and AFM measurements, cf Figures 3 and 4, confirm that the graphene grown in areas initially covered by the mask has good structural quality. By tailoring the growth parameters selective graphene growth (Figures 1,3,4) and sub-micron patterns (Figure 1) have been obtained.

**References**
[1] R Puybaret et al, arxiv.org/abs/1307.6197, 2013
[2] R Puybaret et al, submitted to Phys Rev Appl, 2013
[3] W. A. de Heer, http://smartech.gatech.edu/xmlui/handle/1853/31270, 2001-2009.
[4] W. A. de Heer, C. Berger, and P. N. First, US Patent 7015142, 2006.
[5] C. Berger et al., Journal of Physical Chemistry B, 108(52):19912–19916, Dec 30 2004.
[6] C. Berger et al., Science, 312(5777):1191–1196, May 26 2006.
[7] J. Hicks et al., Nat Phys, 9(1):49–54, JAN 2013.
[8] J. Baringhaus, M. Ruan et al., Nat Phys, arXiv:1301.5354 [cond- mat.mes-hall]., 2013.
[9] Y. M. Lin et al., Science, 327(5966):662, FEB 5 2010.
[10] Z. Guo et al., Nano Letters, 13(3):942–947, MAR 2013.
[11] B. Dlubak, M-B Martin et al., Nat Phys, 8(7):557–561, JUL 2012.
[12] Y.M. Lin et al., Science, 332(6035):1294–1297, JUN 10 2011.
[13] M. Rubio-Roy, F. Zaman et al., Applied Physics Letters, 96(8), Feb 22 2010.
[14] S. Tongay et al., Applied Physics Letters, 100(7), Feb 13 2012.
[15] M. Sprinkle et al., Nat Nano, 5(10):727–731, 10 2010.
[16] W.A de Heer et al., PNAS, 108(41):16900–16905, Oct 11 2011.

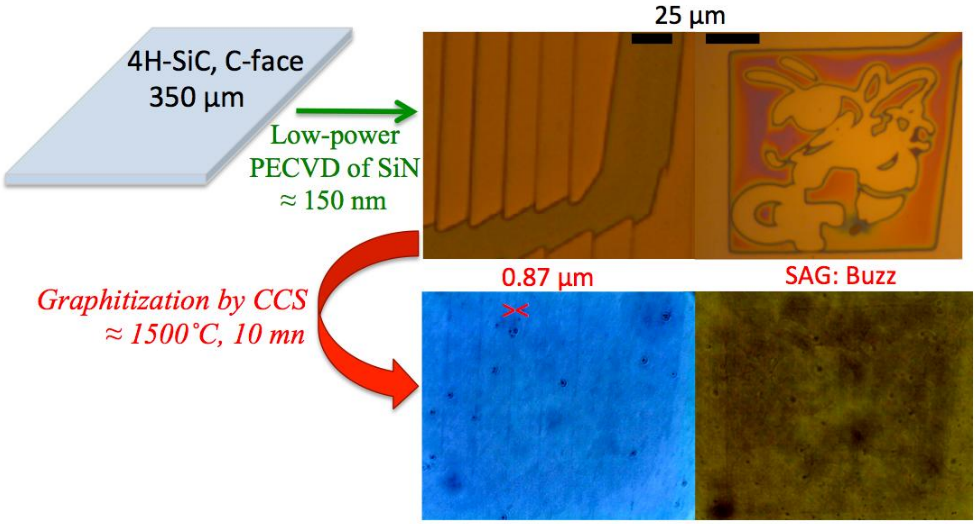


**Figure 1: Overview of the process and optical images of patterns, with the SiN initial pattern of top, the resulting graphene pattern on the bottom, with:**

- *left:* array of ribbons, which graphitized into 3-layer graphene ribbons on 1-2 layer graphene, 0.87 to 1.2 µm wide, 130 µm long.
- *right:* Proof-of-principle pattern of selectively grown graphene on SiC, representing Buzz, Georgia Tech's mascot, darker areas are mono-layer graphene, lighter areas SiC.

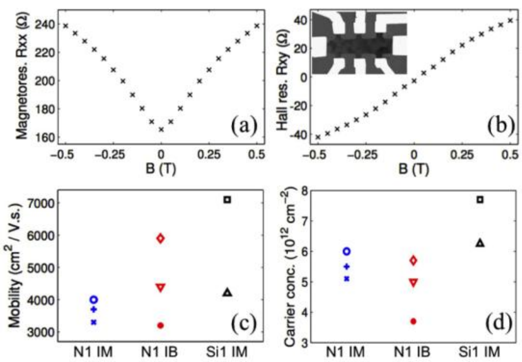

**Figure 2: Transport measurements**

(a) (b): Magneto- and Hall resistances at room temperature of IM area of Si-rich sample: n=7.7 $e^{12}$ $cm^{-2}$ and $\mu$ = 7100 $cm^2 .V^{-1} .s^{-1}$. Hall bar is 3 µm wide.

(c) (d): Mobility and carrier concentrations at room temperature measured on the IM area of N-rich sample, IB area of N-rich sample, and IM area of Si-rich sample.

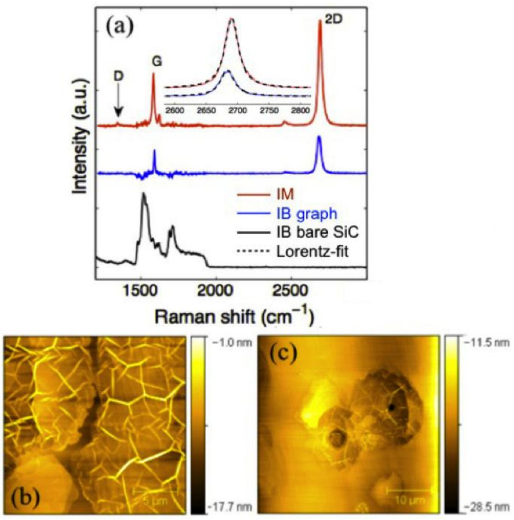

**Figure 3: Si-rich SiN mask, SAG. For this 3.5x4.5 $mm^2$ sample the top half was initially masked (IM) with Si-rich SiN, the bottom half was initially bare (IB)**

(a) Raman spectra (SiC contribution subtracted), showing the typical MEG spectrum. For both graphene spectra the intensity is normalized to the SiC plateau at 1900 $cm^{-1}$, indicating that in the IB areas graphene coverage is much reduced.

Note the quasi absence of D-peak.

(b) AFM image of IM area (scale 20x20 $\mu m^2$).

(c) AFM image of IB area (scale 40x40 $\mu m^2$).

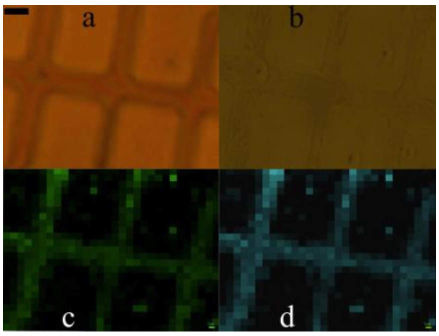

**Figure 4: Selectively-grown two-layer graphene Hall bar using a Si-rich SiN mask, critical dimension 4µm.**

a: SiN pattern. Scale bar is 8 µm.

b: consequent graphene growth.

c: Raman 2D intensity mapping.

d: Raman 2D/G intensity mapping