

Resolving the Controversial Existence of Silicene and Germanene Nanosheets Grown on Graphite

Wenbing Peng^{†,‡}, Tao Xu^{‡,§}, Pascale Diener[‡], Louis Biadala[‡], Maxime Berthe[‡], Xiaodong Pi^{†,*}, Yves Borensztein,[†] Alberto Curcella,[†] Romain Bernard,[†] Geoffroy Prévot,^{†*} Bruno Grandidier^{‡*}

[†] *State Key Laboratory of silicon Materials, and School of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, China*

[‡] *Univ. Lille, CNRS, Centrale Lille, ISEN, Univ. Valenciennes, UMR 8520 - IEMN, F-59000 Lille, France*

[§] *Sino-European School of Technology, Shanghai University, 99 Shangda Road, Shanghai, 200444, People's Republic of China*

[†] *Sorbonne Université, CNRS, Institut des NanoSciences de Paris, UMR 7588, F-75005 Paris, France*

* B. Grandidier. E-mail: bruno.grandidier@isen.iemn.univ-lille1.fr

1) Ge deposition on the HOPG surface at 85°C

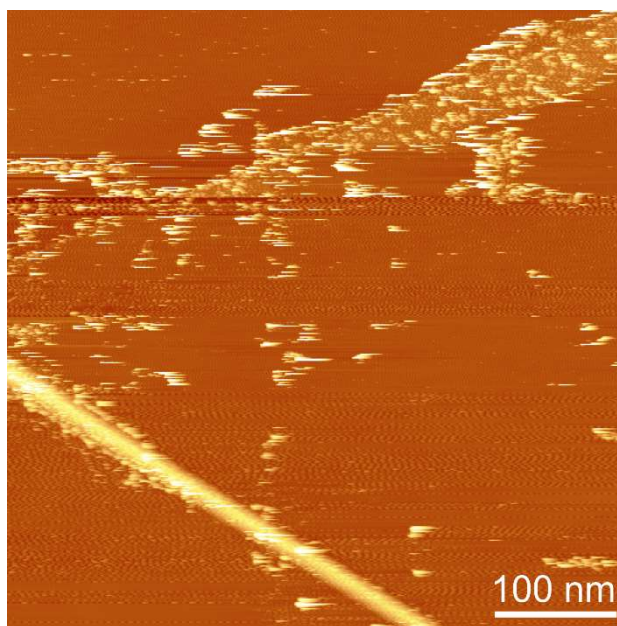


Figure S1: Large scale STM image of the HOPG surface after Ge deposition at 85°C. Tunneling conditions: $V_{\text{bias}} = -2\text{V}$, $I_{\text{setpoint}} = 10\text{pA}$.

2) Apparent height of the Si and Ge clusters

The color scale used for Figure 2 has been expanded to better see the morphology of the cluster labelled A in the main text.

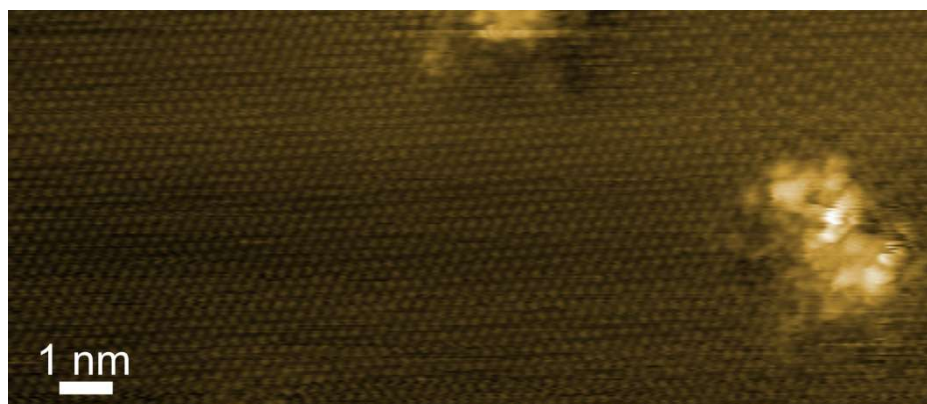


Figure S2. Room temperature STM observation of HOPG after deposition of about 0.2 ML of Si. Tunneling conditions: $V_{\text{sample}}=0.20$ V, $I_{\text{setpoint}}=50$ pA.

Height profiles have been added to Figures 5 and 6 to show the apparent height of the Ge clusters.

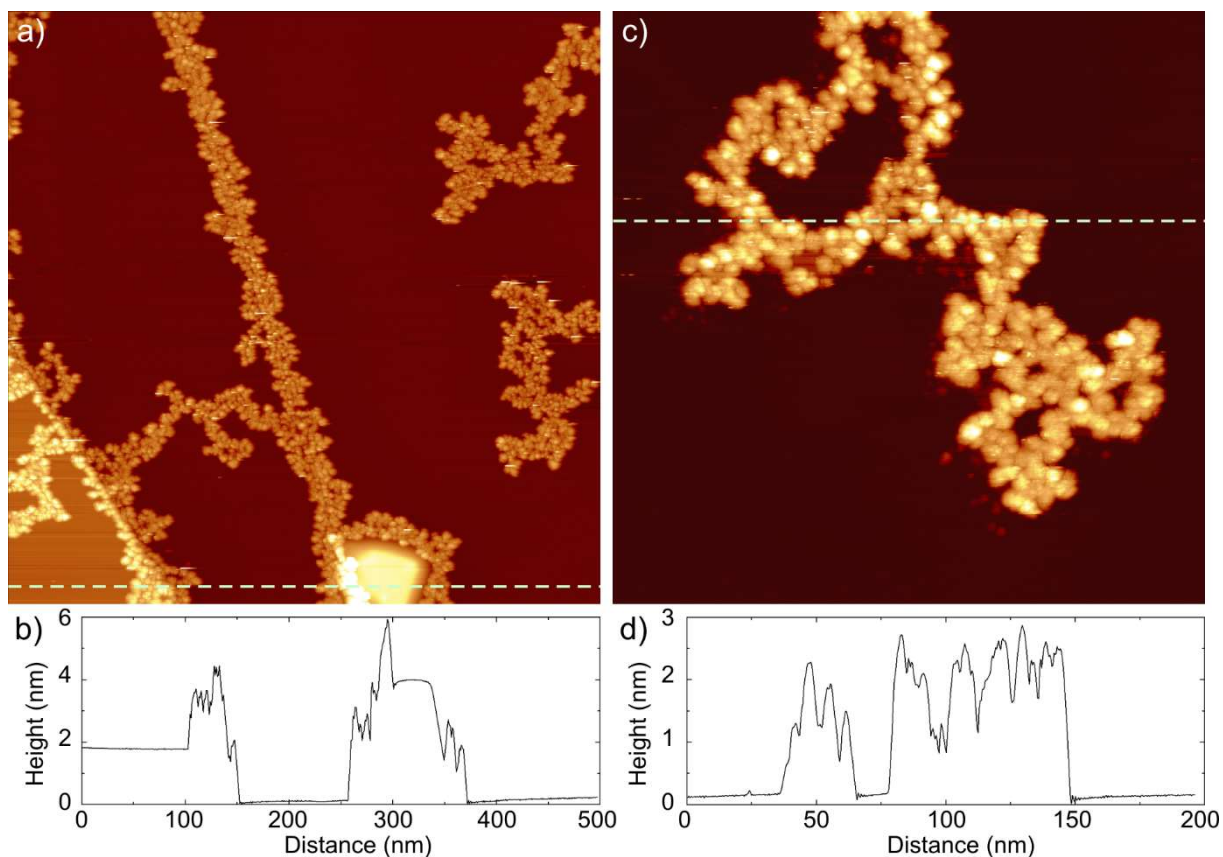


Figure S3. STM images of the HOPG surface after Ge deposition at (a) 120°C and (c) room temperature, corresponding to the STM images shown in Figure 5(a) and 6(a). (b) and (d) Height profiles along the dashed lines shown in (a) and (c).

3) Origin of the observation of small islands on the HOPG surface

It is known that metal atoms intercalate into HOPG.¹ By analogy, Si and Ge atoms could reside between the original graphite layers due to an intercalation process via step edges or defects. In such an area, the change of the electrical conductivity would cause a modification of the STM contrast, giving rise to the occurrence of the small islands observed in Figures 4 and 5. However, in contrast to graphite intercalation compounds, it has been shown that the intercalation of Si and Ge between heteroepitaxial graphite and SiC(0001) requires much higher temperatures than the ones used in this study.^{2,3,4} Alternatively, we suggest that the islands correspond to graphene nanosheets that are cleaved during the exfoliation process. We suspect that they are weakly adsorbed on the HOPG surface, accounting for the absence of their observation, when a clean and bare HOPG surface is characterized with STM. However, upon adsorption of Si and Ge atoms, the edge of the nanosheets can act as nucleation sites, facilitating the formation of clusters that reciprocally stabilize the nanosheets. Figure S4 shows an STM image, obtained after the deposition of 0.2 ML of Si at room temperature, that supports this hypothesis. In contrast to Figure 5, where the density of Ge clusters is high, the density of Si clusters is much smaller. As a result, the clusters do not impede the diffusion of the nanosheets and two nanosheets adsorbed on the atomically flat upper terrace shift laterally, while the STM tip is scanning.

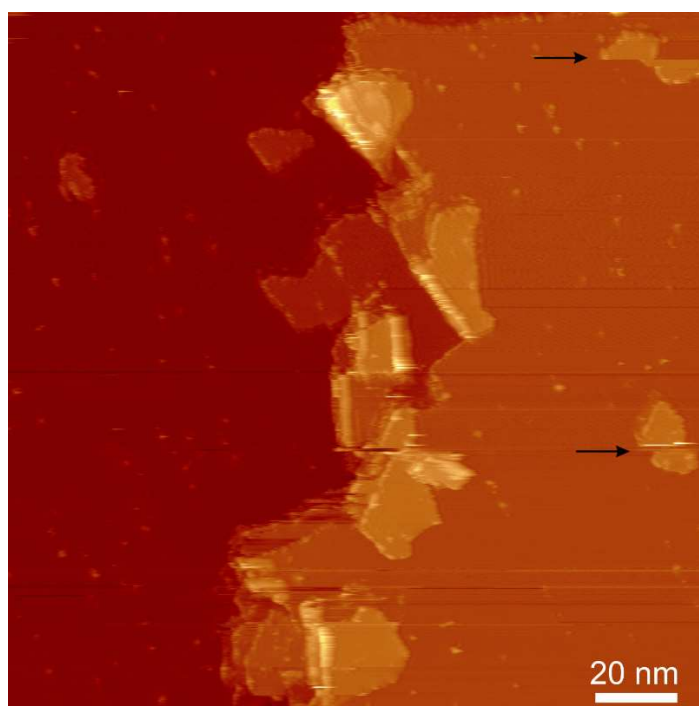


Figure S4. Room temperature STM observation of HOPG after deposition of about 0.2 ML of Si. The arrows point out islands that shift laterally under the STM tip. Tunneling conditions: $V_{\text{sample}} = 0.2 \text{ V}$, $I_{\text{setpoint}} = 50 \text{ pA}$.

4) 1ML deposition of Ge on the Al(111) surface at 110°C

The synthesis of germanene was achieved on the Al(111) surface with identical growth conditions as the ones used for the deposition of Ge on the HOPG surface. Germanium atoms crystallizes in an ordered hexagonal structure with a (3x3) lattice periodicity with respect to Al

(1x1).⁵ Such a structure corresponds to the 1H configuration of germanene, as defined in Ref. 6.

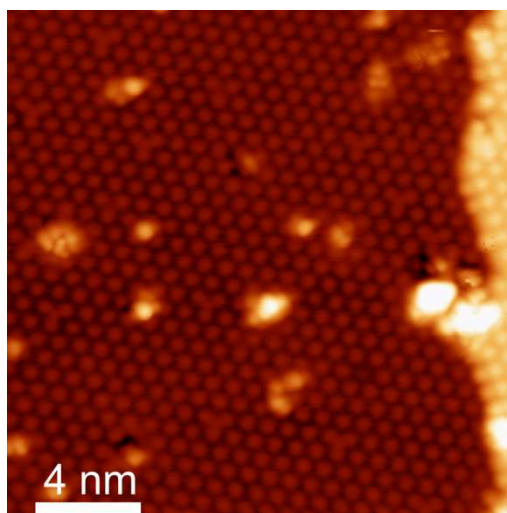


Figure S5: Atomic-resolved STM image of germanene on the Al(111) surface acquired at 77K. Tunneling conditions: $V_{\text{bias}} = -1.0\text{V}$, $I_{\text{setpoint}} = 100\text{pA}$.

-
- (1) Dresselhaus, M. S.; Dresselhaus, G. Intercalation Compounds of Graphite. *Adv. Phys.* **2002**, *51*, 1-186.
 - (2) Xia, C.; Watcharinyanon, S.; Zakharov, A. A.; Yakimova, R.; Hultman, L.; Johansson, L. I.; Virojanadara, C. Si Intercalation/Deintercalation of Graphene on 6 H-SiC (0001). *Phys. Rev. B*, **2012**, *85*, 045418.
 - (3) Kubler, L.; Aït-Mansour, K. ; Diani, M.; Dentel, D.; Bischoff, J. L.; Derivaz, M. Bidimensional Intercalation of Ge Between SiC (0001) and a Heteroepitaxial Graphite Top Layer. *Phys. Rev. B* **2005**, *72*, 115319.
 - (4) Emtsev, K. V.; Zakharov, A. A.; Coletti, C.; Forti, S.; Starke, U. Ambipolar Doping in Quasifree Epitaxial Graphene on SiC (0001) Controlled by Ge Intercalation. *Phys. Rev. B*, **2011**, *84*, 125423.
 - (5) Wang, W.; Uhrberg, R. I. Coexistence of strongly buckled germanene phases on Al (111). *Beilstein J. Nanotechnol* **2017**, *8*, 1946-1951.
 - (6) Stephan, R.; Derivaz, M.; Hanf, M. C.; Dentel, D.; Massara, N.; Mehdaoui, A.; Sonnet, P.; Pirri, C. Tip-Induced Switch of Germanene Atomic Structure. *J. Phys. Chem. Lett.* **2017**, *8*, 4587–4593.