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## Van der Waals Heteroepitaxy of Air-Stable Quasi-Free-Standing Silicene Layers on CVD Epitaxial Graphene/6H-SiC

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► **To cite this version:**

Zouhour Ben Jabra, Mathieu Abel, Filippo Fabbri, Jean-Noel Aqua, Mathieu Koudia, et al.. Van der Waals Heteroepitaxy of Air-Stable Quasi-Free-Standing Silicene Layers on CVD Epitaxial Graphene/6H-SiC. ACS Nano, 2022, 16 (4), pp.5920-5931. 10.1021/acsnano.1c11122 . hal-03841573

**HAL Id: hal-03841573**

**<https://hal.science/hal-03841573>**

Submitted on 7 Nov 2022

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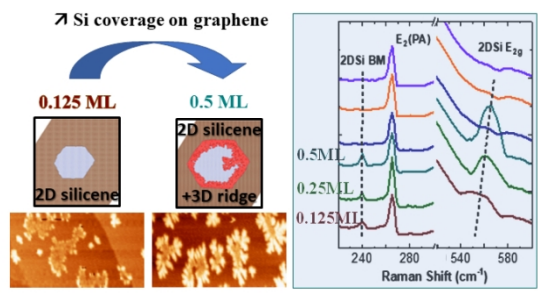
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Journal:	ACS Nano
Manuscript ID	nn-2021-11122u.R4
Manuscript Type:	Article
Date Submitted by the Author:	n/a
Complete List of Authors:	BEN JABRA, Zouhour; AMU, IM2NP Abel, Mathieu; Aix-Marseille Universite, IM2NP Fabbri, Filippo; Istituto Nanoscienze Consiglio Nazionale delle Ricerche, Aqua, Jean-Noël; Sorbonne Université, INSP, UMR 7588 Koudia, Mathieu; Aix-Marseille Universite, IM2NP, Faculté des Sciences et Techniques Michon, Adrien; Universite Cote d'Azur Faculte des Sciences, CNRS, CRHEA, Castrucci, Paola; Università Roma Tor Vergata, Dipartimento di Fisica Ronda, Antoine; CNRS, IM2NP Vach, Holger; Laboratoire de physique des interfaces et des couches minces, De Crescenzi, Maurizio; University of Rome Tor Vergata, Dipartimento di Fisica Berbezier, Isabelle; CNRS - AMU, IM2NP

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# Van der Waals heteroepitaxy of air stable quasi-free standing silicene layers on CVD epitaxial graphene/6H-SiC

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## ABSTRACT

Graphene, consisting of an inert, thermally stable material with an atomically flat, dangling bond-free surface is by essence an ideal template layer for van der Waals heteroepitaxy of two-dimensional materials such as silicene. However, depending on the synthesis method and growth parameters, graphene (Gr) substrates could exhibit, on a single sample, various surface structures, thicknesses, defects, and step heights. These structures noticeably affect the growth mode of epitaxial layers, e.g. turning the layer-by-layer growth into the Volmer Weber growth promoted by defect-assisted nucleation. In this work, the growth of silicon on chemical vapor deposited epitaxial Gr (1 ML Gr/1ML Gr buffer) on 6H-SiC(0001) substrate is investigated by a combination

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3 of atomic force microscopy (AFM), scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy  
4 (XPS), scanning electron microscopy (SEM) and Raman spectroscopy measurements. It is shown that the  
5 perfect control of full-scale almost defect-free 1 ML Gr with a single surface structure and the ultra-clean  
6 conditions for molecular beam epitaxy (MBE) deposition of silicon represent key prerequisites for ensuring  
7 the growth of extended silicene sheets on epitaxial graphene. At low coverages, the deposition of Si produces  
8 large silicene sheets (some hundreds of nanometers large) attested by both AFM and SEM observations and  
9 the onset of a Raman peak at  $560\text{ cm}^{-1}$  very close to the theoretical value of  $570\text{ cm}^{-1}$  calculated for free-  
10 standing silicene. This vibrational mode at  $560\text{ cm}^{-1}$  represents the highest ever experimentally measured value  
11 and is representative of quasi-free standing silicene with almost no interaction with inert non-metal substrates.  
12 From a coverage rate of 1ML, the silicene sheets disappear at the expense of 3D Si dendritic islands whose  
13 density, size, and thickness increase with the deposited thickness. From this coverage, the Raman mode  
14 assigned to quasi-free standing silicene totally vanishes, and the 2D flakes of silicene are no longer observed  
15 by AFM. The experimental results are in very good agreement with the results of kinetic Monte-Carlo  
16 simulations that rationalize the initial flake growth in solid-state dewetting conditions, followed by the growth  
17 of ridges surrounding and covering the 2D flakes. A full description of the growth mechanism is given. This  
18 study, which covers a wide range of growth parameters, challenges recent results stating the impossibility to  
19 grow silicene on a carbon inert surface and is very promising for large scale silicene growth. It shows that  
20 silicene growth can be achieved using perfectly controlled and ultra-clean deposition conditions and an almost  
21 defect-free Gr substrate.  
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35 **KEYWORDS:** 2D materials, Silicene, Graphene, Van der Waals heterostructure, Molecular Beam Epitaxy,  
36 nucleation and growth, kinetic Monte-Carlo  
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## 40 INTRODUCTION

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43 Silicene (Si-ene) represents an ideal 2D material that shares all the outstanding characteristics of graphene  
44 (mainly magnetic, mechanical, optical and electrical properties)<sup>1-7</sup> associated with the additional advantage of  
45 a narrow band gap that can easily be opened by doping,<sup>8-11</sup> by applying external electric and magnetic fields,  
46 <sup>12, 13</sup> and mechanical strain.<sup>14</sup> It also has the significant potential for straightforward integration into industrial  
47 semiconductor production lines, making Si-ene a promising candidate for microelectronic devices.<sup>15-19</sup> Si-ene  
48 has therefore attracted a large amount of studies and has been the subject of intense debates about the origin  
49 of the complex surface superstructures observed as well as its strong interaction with the substrate.<sup>20-24</sup>  
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3 The first evidence of monolayer silicon with anomalous optical properties (optical absorbance at 280 nm and  
4 photoluminescence peak at 434 nm, i.e. 2.9 eV), was given using chemical exfoliation from calcium disilicide  
5 with propylamine hydrochloride<sup>25, 26</sup>. However, it was then reported that unlike Graphene (Gr), Si-ene cannot  
6 be obtained by mechanical exfoliation.<sup>27</sup> Si-ene should then be deposited by molecular beam epitaxy (MBE)<sup>28</sup>  
7 or chemical vapor deposition (CVD).<sup>29</sup>  
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11 The studies on Si-ene initially focused on its growth on Ag(001),<sup>30</sup> Ag(110),<sup>31</sup> and Ag(111) substrates.<sup>20, 32, 33</sup>  
12 The growth of graphene-like Si-ene nanoribbons was first reported. The demonstration of larger Si-ene sheets  
13 was then obtained by a combination of scanning tunneling microscopy (STM), angular-resolved  
14 photoemission spectroscopy (ARPES), and density functional theory (DFT) simulations.<sup>34, 35</sup> However, rapidly  
15 various controversies have emerged about the origin of the various surface reconstructions observed, including  
16  $(4\times 4)$ ,  $(\sqrt{13}\times\sqrt{13})R13.9^\circ$ ,  $(\sqrt{7}\times\sqrt{7})R19.1^\circ$  and  $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$  with respect to Ag(111).<sup>23, 36-38</sup>  
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22 First-principles calculations demonstrated that the linear dispersion band observed by ARPES experiments  
23 could originate from the hybridization states between silicene and Ag(111) surface.<sup>39</sup> Besides, its impressive  
24 stability was definitely ascribed to covalent bonds with the substrate.<sup>21, 40</sup> It was also reported that the Dirac  
25 cone in Si-ene on a Ag(111) surface was destroyed due to the distortion of the Si-ene crystalline cell and strong  
26 band hybridization at the Si-ene/Ag(111) interface by unfolding bands.<sup>41</sup> The linear dispersion observed in  
27 ARPES was then ascribed to the Ag substrate, instead of Si-ene.<sup>39</sup>  
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32 Consequently, the investigations naturally shifted to alternative metal substrates such as Ir(111),<sup>42</sup> Ru (0001),<sup>43</sup>  
33 Pt(111),<sup>44</sup> Pb(111),<sup>45</sup> and Au(111).<sup>46, 47</sup> There again, strong interactions with the substrates were demonstrated  
34 both theoretically and experimentally.<sup>48, 49</sup>  
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38 More recently, to overcome this limitation various experiments have been carried out on C-based inert  
39 substrates such as highly oriented pyrolytic graphite (HOPG) with hexagonal atomic arrangements.<sup>50-53</sup> On  
40 this substrate, the results demonstrated that the charge modulations caused by quantum interferences (QI) serve  
41 as templates and guide the incoming Si atoms to self-assemble in 2D clusters.<sup>54</sup> The restricted extension of  
42 these QI limits the growth to very tiny 2D Si-ene flakes in the nanometer range and causes the transition to a  
43 3D growth mechanism resulting in small 3D clusters at the outskirts of the tiny 2D Si-ene areas as observed  
44 experimentally.<sup>54, 55</sup> The size limitation also originates from the presence of high defect densities on the HOPG  
45 substrate which favor both intercalation of silicon underneath the top surface (even at room temperature)  
46 resulting in the formation of buried silicene<sup>56, 57</sup> and the preferential defect-assisted 3D cluster nucleation at  
47 the origin of the transition between layer-by-layer growth and Volmer-Weber growth.  
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3 The van der Waals (vdW) epitaxy of Si-ene layers with low-buckled honeycomb geometry on graphene-  
4 covered SiC substrates was theoretically demonstrated by first-principles calculations including vdW  
5 interaction in the ground state and quasiparticle effects in the electronic structure.<sup>58</sup> However, similar behavior  
6 (intercalation and 3D cluster nucleation) was also observed during the growth of silicon on graphene  
7 epitaxially grown on Ruthenium<sup>59, 60</sup> or on Ir substrates.<sup>61</sup> At the opposite, a defect-free atomically planar  
8 graphene surface, can act as scaffold to stabilize the growth of 2D materials, enabling construction of 2D  
9 materials that do not naturally exist or are not stable as free-standing films.<sup>62</sup>  
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15 To go beyond and meet the challenges raised by microelectronic devices, semiconducting MoS<sub>2</sub><sup>63, 64</sup> and  
16 insulating h-BN<sup>65</sup> substrates were used for the vdW epitaxy of Si-ene. However, considering the complexity  
17 of obtaining MoS<sub>2</sub> with high quality buffer layers (monocrystalline and free of defects and moirés) and h-BN  
18 over large areas without crystal defects or impurities, the use of such stacked layers seems cumbersome to date  
19 for any potential applications.<sup>66</sup> In summary, since most of the inert substrates have sizeable density of defects,  
20 a general tendency of Si atoms to intercalate during deposition or thermal annealing has been evidenced.  
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25 In this work we have investigated the growth of silicon deposited in ultra-clean Molecular Beam Epitaxy  
26 (MBE) conditions on an almost defect-free graphene layer obtained on 6H-SiC(0001) substrate by an original  
27 CVD process already described elsewhere.<sup>67, 68</sup> We show that two prerequisites are essential for the epitaxial  
28 growth of large scale Si-ene flakes on Gr: first, perfectly flat almost defect-free 1ML Gr and second the ultra-  
29 clean UHV environment during the growth of Si-ene. By a combination of atomic force microscopy (AFM),  
30 STM, x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and Raman spectroscopy  
31 measurements, we demonstrate the formation of 2D quasi-free standing Si-ene flakes on a scale of one-two  
32 hundred nanometers randomly deposited all over the sample surface. In absence of surface defects and  
33 contaminants both on the substrate and in the deposited material, both the diffusion path toward the subsurface  
34 layer and the preferential nucleation of 3D islands are significantly reduced. Without interaction with the Gr  
35 substrate, silicon forms 2D quasi-freestanding flakes whose lateral extension reaches some hundreds of  
36 nanometers. The growth mechanism of 2D Si-ene flakes is explained by kinetic Monte-Carlo (KMC)  
37 simulations that perfectly reproduce and explain the growth morphologies resulting from 2D growth in solid-  
38 state dewetting conditions followed by the growth of 3D ridges surrounding the Si-ene flakes.  
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## 51 RESULTS

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53 Figure 1a shows a STM image of the nominal Gr film on 6H-SiC(0001) (after cleaning at 650°C), where the  
54 Raman measurements in Figure 1d were performed. The absence of defects was observed in numerous large-  
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3 scale AFM and SEM images recorded on each sample (see for instance Figures S1). The morphology presents  
4 terraces separated by a train of steps with 1.5 nm height, which mimics the regular train of 6 silicon carbide  
5 bilayer steps of the 6H-SiC(0001) substrate. The steps are oriented along  $[1\bar{1}00]$  and are constituted of smaller  
6 sections with armchair edges, forming an angle of  $120^\circ$  to each other.<sup>68</sup> Figure 1b gives a STM high resolution  
7 image of the surface structure where the superimposition of the graphene crystalline cell (0.246 nm) and the  $(6$   
8  $\sqrt{3} \times 6\sqrt{3})R30^\circ$  superstructure referring to  $6\sqrt{3}\times\text{SiC}$  cell or 13xGr cell ( $\sim 3.2\text{nm}$ ) is clearly visible. Such a  
9 surface is called (6x6)Gr (6xSiC cell = 1.9nm) in the rest of the manuscript (see Ref. <sup>69</sup> for a detailed  
10 description of graphene ). The corrugation of the top surface is about 0.02 – 0.04 nm in good agreement with  
11 the literature.<sup>70</sup> A complete description of the surface structure and composition of (6x6)Gr can be found in  
12 Ref. <sup>71</sup>. The sample is fully covered by very stable 1ML (6x6)Gr which is free of contaminants and of extended  
13 defects thanks to the cleaning procedure. The presence of point defects cannot be excluded. The XPS peak of  
14 carbon (C1s) gives evidence for the absence of oxygen at the surface (Figure 1c). It can be deconvoluted into  
15 4 different components ascribed to the buffer layer (BL) S1 (284.6eV) and S2 (285.3 eV), to the Gr on top of  
16 the BL (284.2 eV) and to SiC below the BL (283.4 eV) that are representative of Gr on BL on 6H-SiC(0001).<sup>72</sup>  
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<sup>73</sup> The quantification of the Gr coverage has been previously estimated to 1ML (from XPS analysis of the Si/C  
ratio).<sup>68</sup>



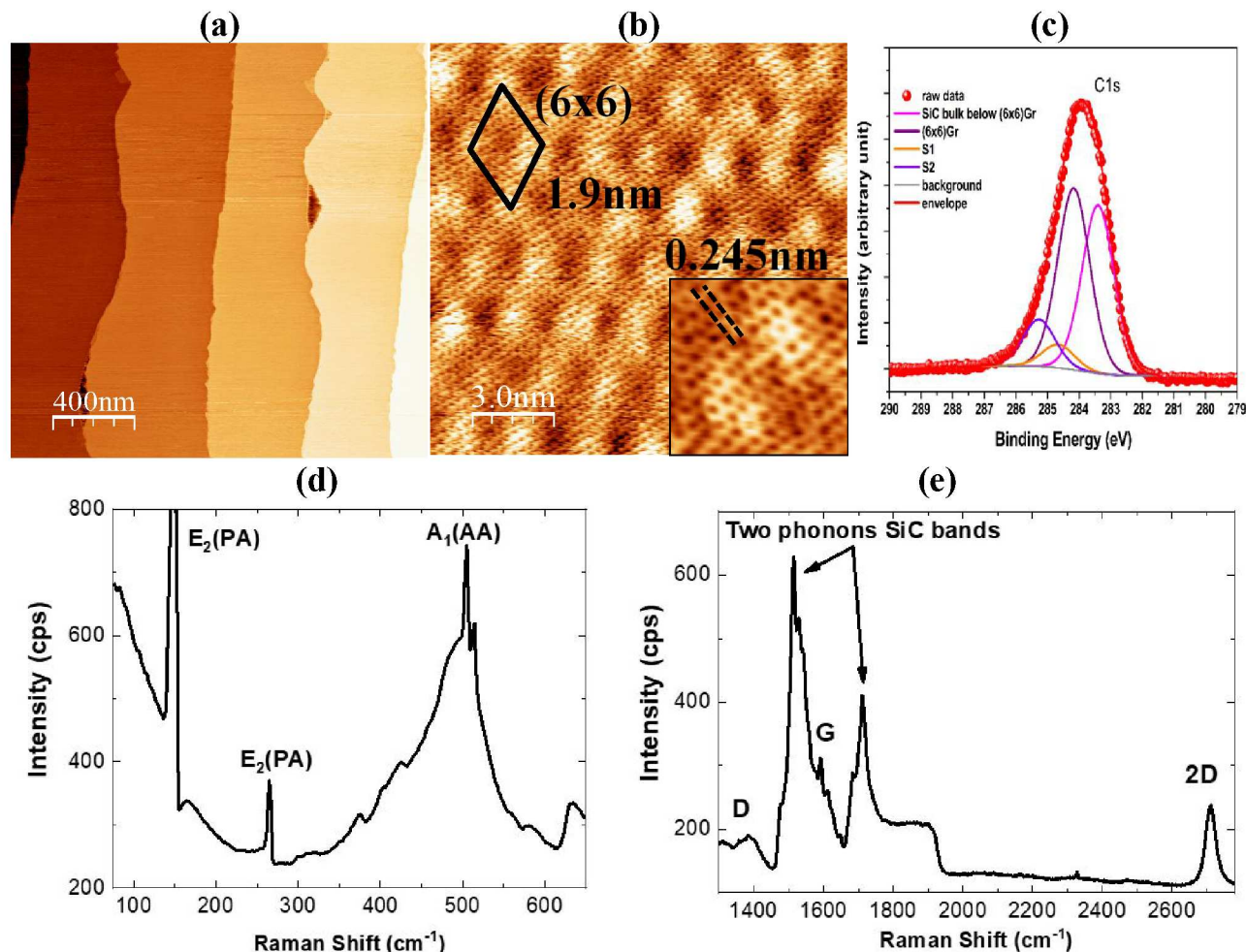
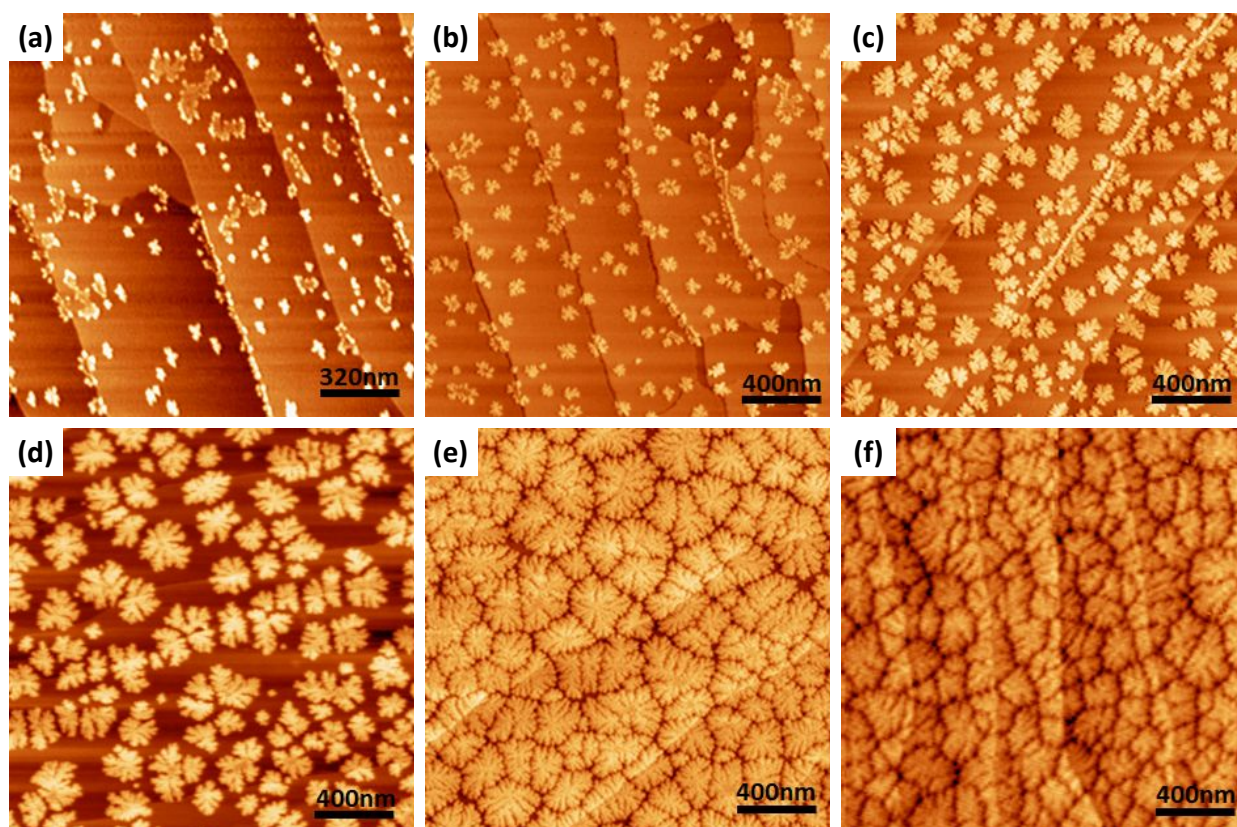


Figure 1: Characterization of the nominal Gr surface after thermal cleaning at 650°C: (a) and (b) STM images of the Gr surface at low and high magnification respectively; (c) XPS spectrum; Raman spectra in the silicon (d) and in the graphene range (e) where the D, G and 2D peaks can be observed together with Raman modes due to the 6H-SiC(0001) substrate.

The Raman spectrum of the epitaxial graphene in the silicon range is shown in Figure 1d, presenting the different Raman features of the 6H-SiC(0001) substrate. In particular, in such a range the different Raman peaks are attributed to acoustic modes: the acoustic planar E2 mode set at 149  $\text{cm}^{-1}$  and at 265  $\text{cm}^{-1}$ , the axial acoustic A1 doublet set at 505  $\text{cm}^{-1}$  and 514  $\text{cm}^{-1}$ .<sup>74</sup> In addition two small peaks at 380  $\text{cm}^{-1}$  and 430  $\text{cm}^{-1}$  can be ascribed to nitrogen doping of the SiC substrate.<sup>75</sup> Raman spectrum in the high Raman shift range, Figure 1e, shows the three fingerprints of the electron-phonon interaction in 2D Gr, i.e. the D peak (at 1358  $\text{cm}^{-1}$ ), the G peak (1591  $\text{cm}^{-1}$ ) and the 2D peak (2712  $\text{cm}^{-1}$ ). The D peak is ascribed to defects associated to step edge orientation in addition to other defects (atomic vacancies, dislocations, grain boundaries) of the substrate and its intensity is related to the concentration of such defects.<sup>76, 77</sup> In the present case, the D/G intensity ratio is rather low. From a careful deconvolution of the peaks of the Figure 1e, it amounts to 0.09, corresponding to a

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4 defect density of  $1.9 \times 10^{10} \text{ cm}^{-2}$ ,<sup>78</sup> i.e. to about one defect over  $10^5$  atoms of the graphene surface value well  
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6 lower than the ratio obtained in exfoliated Gr where it reaches values up to 0.8.<sup>79</sup> In addition, since the D peak  
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8 onset requires intervalley scattering, it appears near a perfect armchair edge (while it cannot be produced by a  
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10 perfect zigzag step edge). This could also explain the presence of the D peak in the (6x6)Gr samples studied  
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12 here that have armchair step edges (as already demonstrated<sup>68</sup>). Such behavior does not apply to the 2D peak,  
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14 not involving intervalley scattering, and that can be activated both by armchair and zigzag edges. The 2D peak  
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16 is the second order overtone of the D peak. The graphene spectrum has a 2D peak with a single Lorentzian  
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18 shape and with a full width at half-maximum  $\text{FWHM}(2D) \sim 35 \text{ cm}^{-1}$ , a signature of single layer graphene on  
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20 a SiC substrate.<sup>80</sup> This result confirms the already reported self-limited graphene growth on top of the BL/6H-  
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22 SiC(0001) which produces 1ML Gr.<sup>68</sup> The G peak corresponds to the doubly degenerate Raman active optical  
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24 vibration E<sub>2g</sub> mode, where the carbon atoms oscillate in the graphene plan. The 6H-SiC(0001) exhibits various  
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26 overtone peaks between 1000 to 2000  $\text{cm}^{-1}$  with some of them superimposed to the peaks of Gr, i.e. the peak  
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28 at 1514  $\text{cm}^{-1}$  which is the overtone of the TO(X) phonon at 761  $\text{cm}^{-1}$  and the peak at 1713  $\text{cm}^{-1}$  which is a  
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30 combination of optical phonons with wave vectors near the M point at the zone edges.



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3 *Figure 2: AFM images of the surface after MBE deposition at room temperature on (6x6)Gr/6H-SiC(0001) substrate*  
4 *of increasing thickness  $\theta$  of silicon : (a) 0.125ML; (b) 0.25ML; (c) 0.5ML; (d) 1MLs; (e) 3MLs; and (f) 6MLs.*

6 During the deposition (at room temperature) of silicon layers of increasing thickness from  $\theta = 0.125\text{ML}$  to  
7 6MLs at a deposition rate of 0.2 nm/min, the morphology of the surfaces changes entirely (Figure 2). The  
8 deposition of 0.125 ML results in small 3D islands and large flat domains, randomly and sparsely distributed  
9 over the surface. The former have an average diameter of  $100\text{ nm} \pm 10\text{ nm}$ . A more detailed observation (zoom  
10 of images in Figures S2 and S3) shows that the larger domains consist of two parts: a flat central area with a  
11 thickness of  $\sim 0.35\text{nm} \pm 0.02\text{nm}$  and lateral dimensions about one-two hundreds of nanometers, surrounded  
12 by small ridges with a mean height of  $1.2\text{nm} \pm 0.2\text{nm}$ . At increasing thickness (0.25 and 0.5ML), the size of  
13 the ridge surrounding the flat areas progressively increases (both laterally and in height) and their dendritic  
14 shape becomes more pronounced. The 2D flat central areas keep constant their lateral dimensions and  
15 thickness up to a 0.5ML coverage, at which they start to be less visible, due to the presence of the ridges (i.e.  
16 higher dendritic islands on their edges). Since the density of the flakes increases with the deposited thickness,  
17 the overall amount of 2D material increases up to 0.5ML. After 1 ML deposition (Figure 2d), the 2D flat areas  
18 totally disappear in favor of 3D dendritic islands and the coverage rate of the surface by dendrites is about  
19 47%. From this 1 ML coverage rate, only the growth of 3D dendrites is observed, resulting in an increase in  
20 dendrites size and height with the deposited thickness. After 3ML deposition (Figure 2e), the surface is fully  
21 covered by dendrites, whose only thickness increases as the amount of the deposit increases up to 6MLs  
22 (Figure 2f). Scanning electron microscopy has been used to confirm the homogeneity of the deposition over  
23 the samples and their morphology (Figure S2). STM characterization of the Si deposition was very  
24 complicated due to contamination of the STM tip by Si clusters. In a few rare cases we obtained images like  
25 the ones reported in Figure S4 of the Supplementary Materials, showing the presence of darker and brighter  
26 regions. Despite the noise on the large scale STM images (Figures S4c and S4d), it is well visible that both  
27 areas are characterized by the superimposition of the two (6x6)Gr and the Gr lattices (Figures S4e and S4f).  
28 Darker regions have a dendritic shape, resembling the shadow of the dendritic islands observed by AFM (see  
29 Figure 2).

30 The elemental and chemical composition of the surface is characterized by XPS. Focus is put on Si2p and C1s  
31 peaks that are recorded at increasing deposited thicknesses of Si (Figure 3). First, it can be noted that the C1s  
32 peak remains constant throughout the growth process and regardless of the deposited thickness (Figure 3a),  
33 with the position and shape of (6x6)Gr already described above and with a similar deconvolution into 4  
34 components (S1, S2, SiC bulk and top layer Gr). The absence of any disturbance (shift or shoulder) of this  
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3 peak is a first indication of a very weak interaction of the Gr substrate with the Si coating. On the other hand,  
4 most of the Si2p peak ( $\sim 101.3\text{eV}$ ) observed comes from the SiC substrate. At the coverage of 3MLs, the  
5 appearance of two shoulders is well visible. They are ascribed to a SiO<sub>x</sub> peak at 102.3eV and the Si bulk at  
6 99.2eV. The Si2p peak evolution has been studied in detail in the Supplementary Materials (see Figures S5).  
7 This analysis shows that the Si and SiO<sub>x</sub> peaks (around 99-99.5 eV and 102.6- 103.4eV respectively) start to  
8 be detectable for Si coverage about 0.5ML where in parallel, the dendritic ridge becomes well visible. Probably  
9 the air resistance of the silicence sheets is due to the passivation of the flake edges by these dendritic structures.  
10 Due to their 3D silicon crystallinity the ridges act as getter for the oxygen, having a preferential oxidation of  
11 such structures. The areas of the SiO<sub>x</sub> and Si bulk peaks increase with the Si coverage becoming more and  
12 more visible for the 3 and 6 ML. At these coverages, the intensity ratio between the SiC substrate peaks and  
13 the Si and SiO<sub>x</sub> peaks decreases hugely due to the formation of a quasi-continuous layer of 3D dendrites  
14 oxidized during air exposure. According to literature,<sup>81, 82</sup> the Si 2D-peaks on inert substrates are expected  
15 around 99-99.5 eV, i.e. at very close energy to the clean Si 3D-peaks. So, it is not straightforward to distinguish  
16 the 2D from the 3D clean Si 2p XPS peaks. Therefore, we suggest that the signal located around  $99.5 \pm 0.3$   
17 eV can be ascribed to both the Si-ene flakes and the 3D dendrites. This is consistent with the AFM analysis  
18 which evidences, even for the lowest Si coverages, the presence of Si-ene flakes surrounded by  $\sim 1\text{nm}$  thick Si  
19 ridges.  
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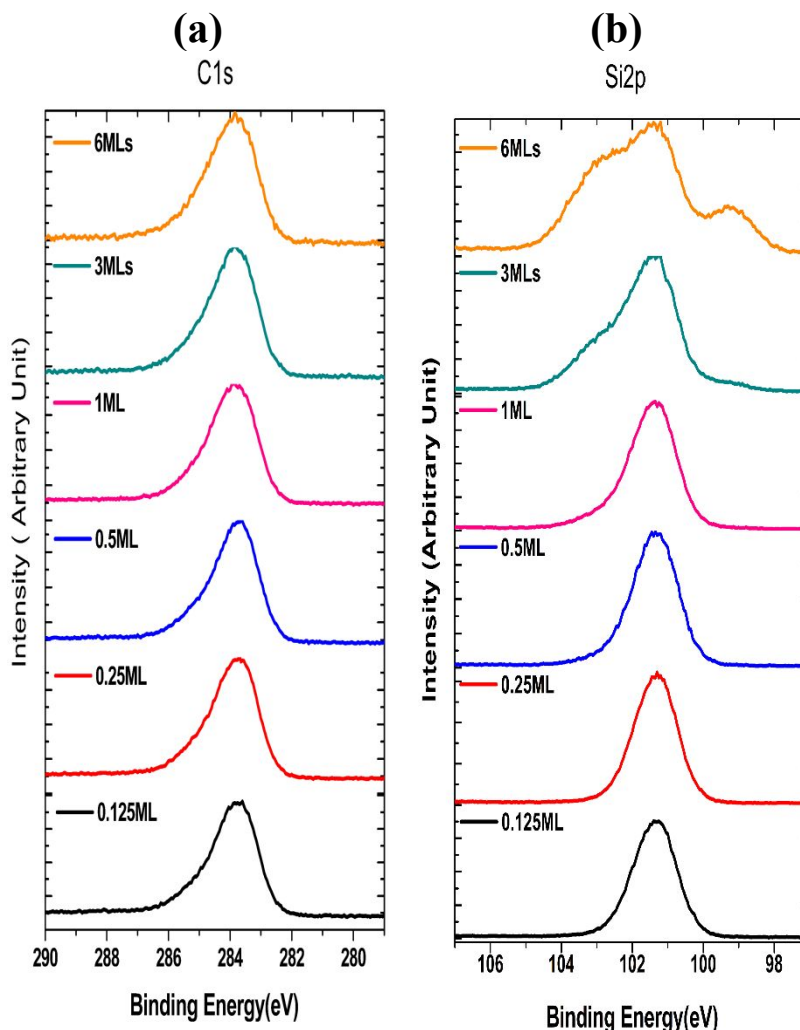


Figure 3: XPS spectra of Si thin films of different thicknesses from 0.125, to 0.25, 0.5, 1, 3, and 6MLs: (a) C1s and (b) Si2p core-level peaks.

Figure 4a displays the Raman spectra for Si layers with different coverages grown on the (6x6)Gr layer. The first-order asymmetric peak located at  $520\text{ cm}^{-1}$  can be assigned to the 6H-SiC(0001) substrate. For small coverages ( $< 1\text{ ML}$ ) two new peaks appeared: one at  $560\text{ cm}^{-1}$  which is interpreted as the zone-center E<sub>2g</sub> vibrational mode of Si-ene (equivalent to the so-called G-like peak of Gr), which was predicted by theoretical studies at  $570\text{ cm}^{-1}$ <sup>34</sup> and another at  $240\text{ cm}^{-1}$  which is assigned to the breathing mode (a zoom of the two peaks is given in Figure 4a). A breathing mode at  $230\text{ cm}^{-1}$  was already reported for Si-ene on Ag. It was correlated with the out-of-plane displacement of Si-atoms that is generated by the buckling.<sup>83</sup> Its intensity is affected by the quantity and nature (zigzag or armchair) of step edges in the Si-ene flakes and we can expect that a higher density of 2D Si-ene flakes produces a peak with higher intensity. In this series of experiments, its intensity slightly increases up to 0.5ML until it completely disappears at 1ML, as shown in Figure 4b. A

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3 similar evolution is observed for the E2g peak: it increases with coverage rate up to 0.5ML where it reaches  
4 its maximum, before it disappears at 1ML coverage. The absence of any silicon related Raman modes at high  
5 coverage (>1ML) suggests the oxidation of the silicon deposited on the surface. The two peaks are absent for  
6 larger coverages, meaning that Si-ene is only formed at small deposited thicknesses (<1ML). These results are  
7 in good agreement with the AFM images of the surfaces (Figure 2) where 2D flakes are well visible until  
8 0.5ML coverage, from which on they totally disappear. We can then conclude that the 2D flakes visible on the  
9 surfaces are composed of 2D quasi-free-standing Si-ene.  
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15 The increase of the E2G peak intensity until 0.5ML (Figure 4b) is most likely induced by an increase of the  
16 quantity of Si-ene (well visible on Figures S2 and S3). Nevertheless, with such low coverage rates (0.125, 0.25  
17 and 0.5) and quite inhomogeneous areas distribution, it is very uncertain to give a quantitative estimate of the  
18 Si-ene coverage on the surface.  
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22 The E2g peak of Si-ene is observed at a frequency very close to the free-standing peak confirming the very  
23 low interaction of the Si-ene flakes with the epitaxial graphene. In addition, as it has been already reported,  
24 the E2g mode in 2D materials can also be modulated by strain and doping.<sup>34</sup> In the case of Si-ene on Ag, the  
25 E2g peak is located at  $530\text{cm}^{-1}$  because of its strong interaction with the substrate which is obviously not the  
26 situation here.<sup>84</sup> In the case of Si-ene nanosheets on HOPG substrate, the E2g mode is located around  $542\text{cm}^{-1}$   
27 because of the relaxation of the Si-Si bond length due to removal of the periodic constrains for an infinite Si-  
28 ene layer with respect to the surface underneath .<sup>51</sup>  
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34 In addition, the Raman shifts of the E2g and breathing mode are reported in Figure 4c. It is worth noting that  
35 the breathing mode Raman shift remains at  $240\text{cm}^{-1}$  for different silicon thicknesses, supporting the attribution  
36 to the out-of-plane displacement of silicon atoms<sup>83</sup>, while the E2g Raman shift increases linearly with the  
37 silicon coverage from  $558\text{cm}^{-1}$  (0.125 ML) up to  $563\text{cm}^{-1}$  (0.5 ML). This is an indication that, with the  
38 enlargement of the lateral size of the Si-ene flakes, their interaction with the substrate decreases leading the  
39 E2g Raman shifts towards the freestanding value of  $570\text{cm}^{-1}$ . It could also be explained by the presence of  
40 oxidized Si islands at the periphery of the domains which could affect the strain and doping of the Si-ene flake.  
41 The error bars reported in Figure 4b and 4c are obtained by statistical analysis of  $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$  Raman maps.  
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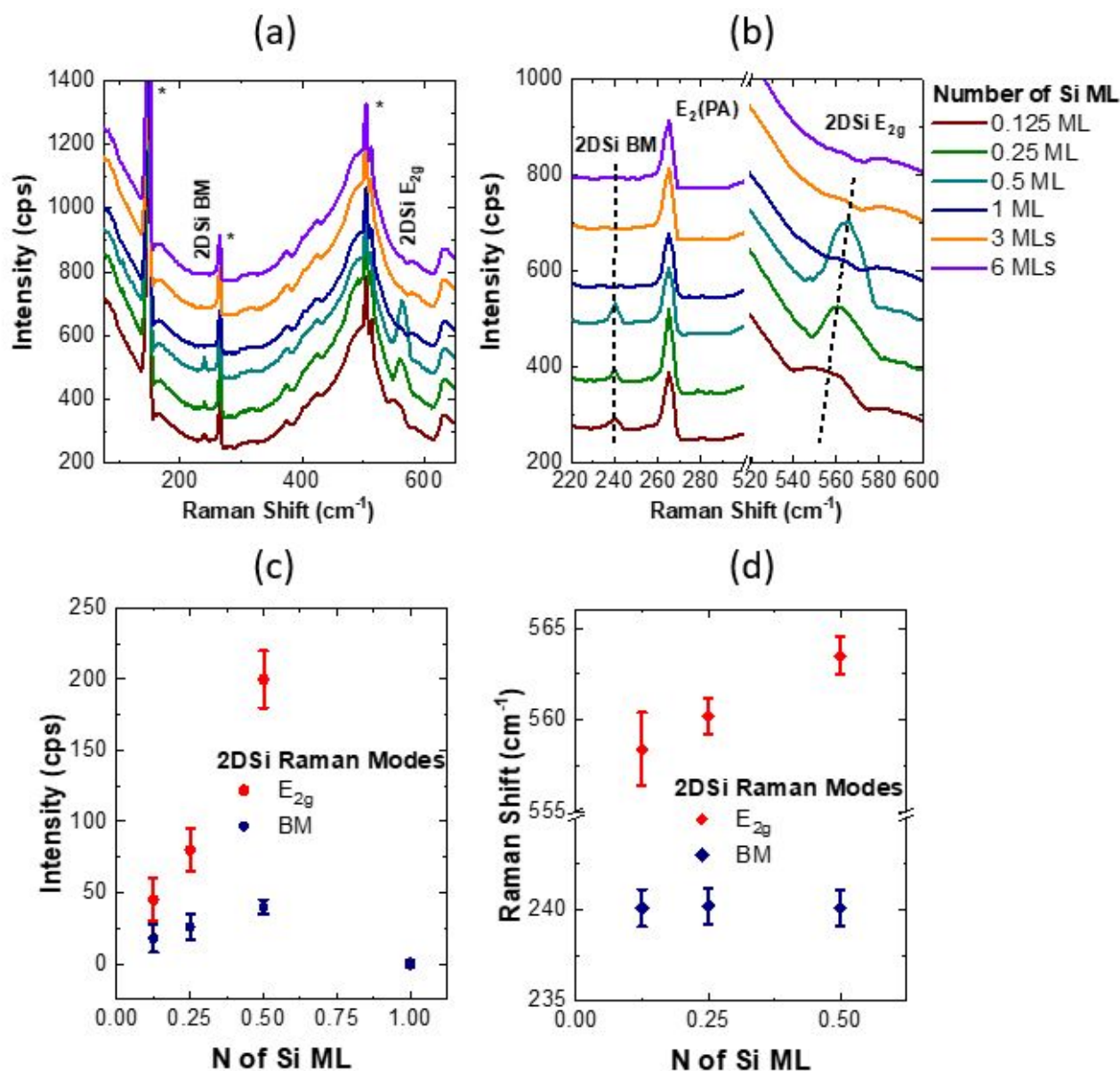


Figure 4: Raman spectra of Si/(6x6)Gr/6H-SiC(0001) with 0,125, 0,25, 0,5, 1, 3 and 6ML coverage: (a) silicon vibrational range of the major Raman features of silicene. Asterisks denote the SiC Raman modes. Evolutions of the 2D Si-ene mode (b) intensity and (c) shift.

The evolution of the Raman spectrum of epitaxial graphene with increasing coverage of silicon is shown in Figure 5a. The main modifications of the graphene Raman modes are: the broadening of the 2D mode, as summarized in Figure 5b, and the shift of the G and 2D modes. In particular, the full width at half maximum (FWHM) of the 2D mode increases with the increase of the silicon coverage, going from 35 cm<sup>-1</sup> for the 0.125 ML up to 38 cm<sup>-1</sup>. The error bars reported in Figure 5b are obtained by statistical analysis of Raman maps obtained in a 20 μm x 20 μm sampling area. The broadening of the 2D peak is assigned to nanoscale strain

effects on the graphene layers.<sup>85</sup> Considering the low interaction of the Si-ene sheets obtained on the graphene surface, it is possible that the strain effects are induced by the presence of the dendritic structures, and in fact this effect dominates for the 3 ML and 6 ML coverages, where Si-ene is completely absent and a complete coverage with a dendritic layer is observed. A similar behavior is reported in the correlation plot of the Raman shift of the G peak with the one of the 2D mode (Figure 5c). The dispersions with different silicon coverages reveal that the n-type doping of epitaxial graphene slightly decreases, while an important spreading is present in all the set of data along the strain direction. This decrease of the electron doping concentration can be due to interface states of oxidized silicon at high silicon coverage.<sup>86</sup> The slope of the linear fitting for the different dispersions varies between 1.2 up to 1.7 that is an indication for biaxial strain of the graphene layer, which is expected due to the complex interaction between graphene and the dendritic structures.<sup>87</sup>

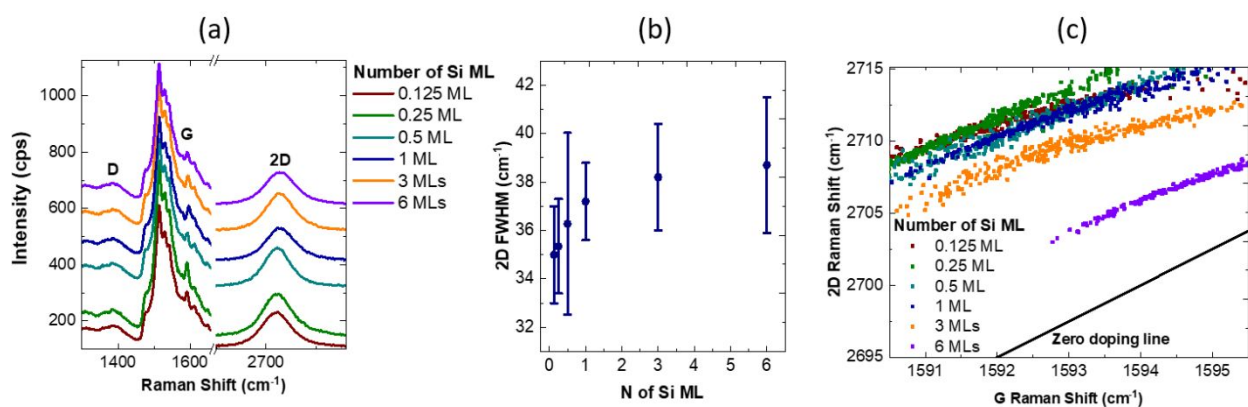


Figure 5: Raman spectra of Si/(6x6)Gr/6H-SiC(0001) with 0,125, 0,25, 0,5, 1, 3 and 6MLs coverages: (a) vibrational range of the major Raman features of graphene. (b) Evolution of the FWHM of the 2D mode as function of the silicon coverage. (c) Strain/doping correlation plot of epitaxial graphene with increasing silicon coverage.

We have then annealed Si-ene samples to better understand the mechanism of formation and stabilization of thin Si-ene areas surrounded by 3D dendrites. Annealings were performed (both in situ just after Si deposition and in another UHV setup after the samples have been exposed to air) for samples with a deposited thickness of 0.5 ML since the most intense Raman peaks resulting from the most extended 2D Si-ene areas are obtained at this coverage. After deposition, all samples showed evidence for large flakes of Si-ene (with lateral sizes up to one-two hundreds of nm) with compact almost hexagonal shapes surrounded by dendritic 3D islands (Figure 6a). On some AFM images, it is also well visible that the Si-ene “floats” on top of the Gr substrate without interacting with it, as can be seen on inset of Figure 6a, where a flake is straddling two terraces like a sheet laid on the step edge. A typical example of the morphology obtained after 2h annealing at 850°C is given on Figure 6b., The density, size and shape of the 2D flakes do not evolve with annealing, but their edges become



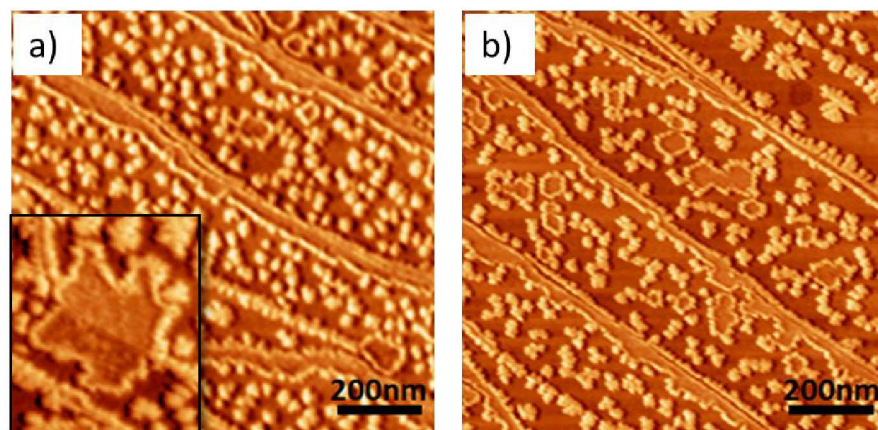


Figure 6: AFM images of the surface after 0.5ML Si deposition at RT: (a) just after growth; in the inset is presented the image of a Si-ene flake straddling two terraces; (b) after 2h annealing at 850°C. The corresponding STM images of this sample are presented in figure S4.

straighter following directions at  $120^\circ$  from each other, which further emphasizes their pseudo-hexagonal shape representative of higher quality crystalline flakes (Figure 6b). The height of the compact planar areas remains in the range of 0.2 – 0.3nm.

The initial steps of the Si-ene flake growth (2D domains followed by 2D domains with a ridge) may be perfectly rationalized by an epitaxial growth mode dictated by solid-state dewetting.<sup>88</sup> We show evidence for such a mechanism thanks to kinetic Monte-Carlo simulations of the epitaxial dynamics. We consider a model geometry with a Solid On Solid (SOS) model where the atomic columns are defined on the basis of the Gr honeycomb lattice. A constant deposition flux  $F$  allows the deposition of Si on Gr. Meanwhile, the top-most atoms are allowed to diffuse with a diffusion energy barrier  $E_S$  and to detach from their  $n$  nearest-in-plane neighbors with a bonding energy barrier  $E_N$ . In this case, the diffusion and detachment processes occur with a frequency proportional to  $\exp[-\beta(E_S + nE_N)]$ . Importantly, the energy barriers  $E_S$  and  $E_N$  are supposed to be function of the local height  $h$ . This is characteristic of wetting conditions where excess quantities depend on the local environment, and especially on the thickness here. This crucial assumption happens naturally here because the Si atoms on the first layer are only weakly bounded to the Gr layer via van-der-Waals interactions. On the contrary, Si atoms diffusing on top of already deposited Si atoms are expected to experience a greater energy barrier due to their covalent bonding with underlying Si atoms. These barriers are thence a priori function of the atomic height, until they reach their values on bulk Si beyond a given thickness (typically beyond 3 or 4 monolayers).<sup>89</sup> The diffusion barrier of Si on Gr was computed to be as low as 0.06 eV on the basis of ab-initio calculations.<sup>90</sup> It is indeed much lower than the usual diffusion barrier of Si on Si(001) that

was measured to be 0.7 eV.<sup>91</sup> The system is highly anisotropic and the dependence of  $E_N$  on  $h$  is less documented. However, for the special case of Si on top of Si(001) with anisotropic type-A and B terraces, it was typically estimated at 0.5 eV by comparison of the results of such a SOS model with anisotropic experimental morphologies on Si(001).<sup>92</sup> We thence considered that  $E_S$  and  $E_N$  vary over  $h=1$  and 2 and stay constant for  $h \geq 3$ . We fixed  $E_S (h=1) = 0.06$  eV and  $E_S (h \geq 3) = 0.7$  eV and considered typically  $E_S (h=2) = 0.08$  eV, while we set  $E_N (h) = 0.4, 0.5$  and  $0.6$  eV for  $h = 1, 2$  and  $3$ , respectively. The resulting evolution is displayed in Figure 7.

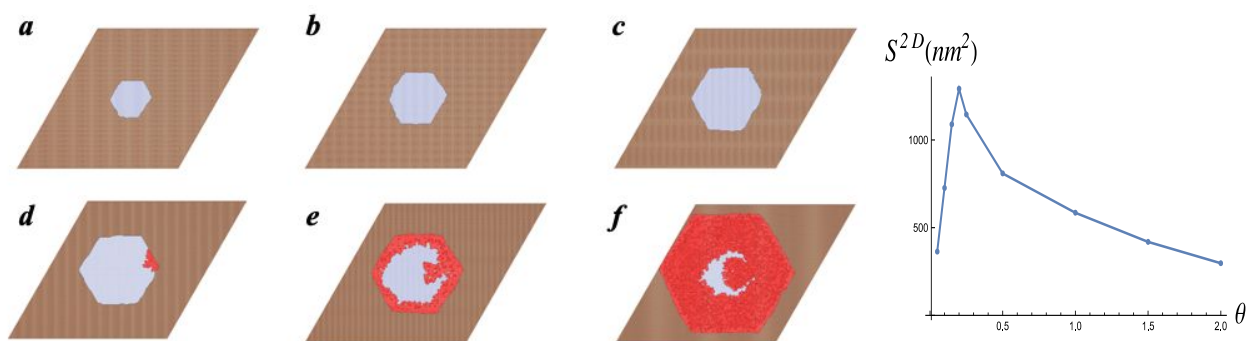


Figure 7: (left) Morphologies of KMC simulations of a SOS-model with thickness-dependent diffusion  $E_S$  and binding energies  $E_N$  at room temperature for the typical parameters described in the text and for coverage Si amount  $\theta =$  (a) 0.05, (b) 0.1, (c) 0.15, (d) 0.2, (e) 0.5 and (f) 2.0 ML (the system size is 200 x 200 graphene lattice parameters, brown region). (right) Evolution of the surface of the 2D flakes as a function of  $\theta$ .

Initially, growth proceeds by the enlargement of a flake that remains perfectly flat and 2D (Figure 7a-c). From a typical coverage of  $\theta^*$ , and for flake sizes of the order of 100 lattice parameters, a ridge starts to form on one edge of the flake. It is noticeable that this localized ridge perfectly corresponds to the geometries initially observed experimentally (Figure 2a). Once formed, the ridge quickly spreads over the entire flake edge and then thickens slowly. At  $\theta=0.5$ ML (Figure 7e), the 2D zone with a thickness  $h=1$ ML is entirely surrounded by a ridge that has a typical thickness of 2 to 3 ML, once again in accordance with the flakes observed experimentally. The precise values of  $\theta$  where the latter steps occur depend on statistical fluctuations, but we observe that the ridge is usually fully formed at 0.5ML. As deposition proceeds, the 2D flake is gradually shrinking and the ridge progressively occupies the entire flake, as can be evidenced by the evolution of the 2D central zone in Figure 7e-f. We thence argue that the so particular flakes and ridges morphologies observed experimentally result from the epitaxial growth dynamics of 2D systems with dewetting conditions depicted by our model. The values of the energy barriers considered here are therefore adequate to account for the experiments, and this result can be considered as a validation or at least an indication of their real values. Important variations of these barriers could, indeed, lead to other growth modes: a plane-by-plane growth; a

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3 fast dewetting leading to compact rough and thick shapes, etc. A detailed study of the different morphologies  
4 potentially contained by this model will be given elsewhere. Another parameter of the model concerns the  
5 initial nucleation of the 2D flakes. We considered here a perfectly homogeneous nucleation on a flat surface  
6 without defect. This corresponds to 2D flakes located on the terraces. For the flakes that overflow from one  
7 terrace to another and cross an atomic step, we can intuit that their nucleation was initiated at the step. While  
8 this geometry does not fundamentally change the mechanism of a de-wetting growth dynamic, it may affect  
9 the densities of islands which will be the subject of a future study.  
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15 The above modeling is dedicated to the 2D flake and ridge formation and does not capture the dendritic growth  
16 that would require a full description of the Si aggregate growth. The mechanism of transition from 2D to 3D  
17 dendrites in MBE growth is poorly understood, even if in general it is correlated to the growth rate and  
18 deposition flux. Here the situation is very complex since Si is supposed to have a very high diffusion length  
19 on Gr even at RT,<sup>90</sup> and there is a huge anisotropy of interaction between the strong Si-Si lateral bonds and  
20 the weak interaction perpendicular to the surface. When the 2D compact domains reach a critical size, the rate  
21 at which the adatoms arrive at the domain edges becomes higher than the edge diffusion that becomes  
22 insufficient to ensure the rearrangement of all incoming adatoms to a stable geometrical configuration. This  
23 promotes the branching along the directions of the domain expansion, leading to dendritic Si domains. For this  
24 reason, the compact area will ramify into branched structures whose primary branches roughly follow a  
25 pseudo-hexagonal shape. For larger dendritic structures, with elongated branches, the adatoms agglomerate  
26 following a diffusion limited process which produces a thickening and disorientation of the branches and the  
27 3D growth prevails. The structural transition can then be attributed to the difference between the rate of adatom  
28 attachment to the edge of the growing nuclei, the rate of edge diffusion and to the strong anisotropy of the  
29 Si-Si interactions between the lateral and the vertical ones. At increasing thickness, the morphology evolves  
30 with a densification and thickening of the 3D dendrites accompanied by an increase of their size. A  
31 comprehensive study on the growth mechanism of the 3D silicon dendrites will be the topic of a future work.  
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## 50 CONCLUSION

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52 Our results provide a clear proof and a complete explanation of the van der Waals epitaxy of 2D Si-ene flakes  
53 on (6x6)Gr on 6H-SiC(0001), when using ultra-clean MBE deposition technique and almost defect-free  
54 graphene substrate. The 2D Si-ene flakes are well identified by AFM images for low silicon deposition  
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3 thickness (<1ML). The presence of 2D flat areas straddling two terraces like a sheet laid on the step, gives a  
4 first indication that the Si-ene flakes “float” on top of the Gr substrate without interacting with it. The 2D  
5 domains are surrounded and progressively covered by 3D ridges forming dendritic islands. At 1ML deposition  
6 they entirely cover the surface at the expense of the 2D flakes. The formation of large scale Si-ene flakes is  
7 also unambiguously attested by Raman spectra which evidence the vibrational modes ascribed to Si-ene: the  
8 zone-center E<sub>2g</sub> vibrational mode at 560 cm<sup>-1</sup>, which was predicted by theoretical studies at 563-570 cm<sup>-1</sup>  
9 (depending on the doping) for free-standing Si-ene and the breathing mode at 240 cm<sup>-1</sup> which is correlated to  
10 the out-of-plane displacement of Si-atoms generated by the buckling. The intensity of these two peaks, which  
11 is related to the quantity of Si-ene flakes, increases up to 0.5ML where the peaks reach their maximum until  
12 they completely disappear at 1ML. The absence of these two peaks for larger coverages, indicates that Si-ene  
13 areas are only present on the surface for small deposited thicknesses (<1ML).  
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22 The growth of the Si-ene flakes followed by 2D domains with a surrounding ridge is well explained by Kinetic  
23 Monte-Carlo simulations when considering highly anisotropic barriers i.e. a factor 10 difference between the  
24 diffusion energy barrier (E<sub>S</sub>) and bonding energy barrier (E<sub>N</sub>). These barriers are also function of the atomic  
25 height, until they reach their values on bulk Si beyond a critical thickness (3-4ML). The first layer of Si atoms  
26 which is only weakly bounded to the Gr layer via van-der-Waals interactions has a very low diffusion barrier  
27 (set at 0.06eV on the basis of ab-initio calculations). On the contrary, Si atoms diffusing on top of already  
28 deposited Si atoms are expected to have a greater energy barrier due to their covalent bonding with the  
29 underlying Si atoms (0.7eV was measured on Si(001)). A similar height dependent evolution of E<sub>N</sub> is also  
30 considered. In these conditions, it is shown that the growth proceeds by the enlargement of a flake that remains  
31 perfectly flat and 2D up to a typical deposited thickness, above which a ridge starts to form on the edge of the  
32 flake. Once the ridge is formed, it quickly spreads over the entire flake and then thickens slowly. The model  
33 demonstrates that the so particular flakes and ridges morphologies observed experimentally result from the  
34 epitaxial growth dynamics of 2D systems with dewetting conditions.  
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43 Our results elucidate the mechanism of formation of Si-ene and provide an efficient and simple way to produce  
44 high-quality and large-scale material on an inert and well-ordered surface. The work also enables investigation  
45 of quantum phenomena, topological insulator behavior towards reliable integration in devices with huge  
46 potential applications in nano-electronics, optoelectronics, and photonics.  
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## 50 METHODS

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53 Graphene samples were grown on the Si-terminated face of Silicon Carbide (6H-SiC(0001)) in a horizontal  
54 hot wall CVD reactor. The 6H-SiC(0001) substrates are on-axis n-doped (nitrogen) 2” wafers with typical  
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3 thickness of  $\sim 350$   $\mu\text{m}$  from Tankeblue. Typical residual offcuts are between  $0.05$  and  $0.2^\circ$  toward the  $[1\bar{1}00]$   
4 direction, as deduced from AFM measurements on annealed substrates under  $\text{H}_2$ .<sup>93</sup> Before introduction into  
5 the growth chamber, the substrates are cut into  $1 \times 1 \text{ cm}^2$  pieces and then chemically cleaned with isopropanol.  
6 Graphene deposition was carried out in a horizontal CVD reactor allowing a homogeneous and reproducible  
7 deposition of Gr on the substrates, at a pressure of 800 mbar using a gas mixture of propane ( $\text{C}_3\text{H}_8$ ) as the  
8 carbon source, and hydrogen ( $\text{H}_2$ ) and argon (Ar) as the carrier gases. The  $\text{H}_2$  flow ratio ( $\text{H}_2$  flow / total flow)  
9 was set to 9% which ensures a surface totally covered by 1ML Gr on top of the buffer layer with the  $(6\sqrt{3} \times 6$   
10  $\sqrt{3})\text{R}30^\circ$  reconstruction (i.e. partly bonded to the SiC substrate).  
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17 The samples completely covered with the 1ML epitaxial Gr are introduced into a perfectly clean ultra-high-  
18 vacuum (UHV) molecular beam epitaxy (MBE) growth chamber dedicated to Si-based heterostructures.  
19 Various set of Si depositions were performed on two different types of epi-Gr grown on hexagonal SiC(0001)  
20 substrates. The substrates are characterized by two different density of defects according to Raman results (i.e.  
21 with different ratios between the intensity of the D and G graphene modes). On these two different substrates,  
22 the Si atoms deposited at room temperature on the epi-Gr give rise to different behaviors. In the present study,  
23 with D/G intensity ratio is around 0.09, i.e. high graphene quality, we obtained wide Si-ene regions, while in  
24 the case of D/G intensity ratio, reaching values up to 0.25, the Si atoms tend to penetrate the epi-Gr layer and  
25 form Si-ene intercalated nanosheets.  
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32 In addition, we also tested the effect of the Gr substrate cleanliness: when the substrate does not undergo any  
33 thermal cleaning, the silicon atoms form a rough amorphous layer of silicon without any Si-ene flakes (Figure  
34 S6).  
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38 The Gr samples are then first thermally cleaned at  $650^\circ\text{C}$  for 120 min. Then the heating is switched off and  
39 the samples are cooled down to room temperature during 180 min before silicon deposition. Silicon is  
40 deposited on the samples at room temperature using an electron beam evaporator, maintaining a constant  
41 deposition rate with uniformity of 5% on the whole sample (with sample rotation). The silicon flux was set to  
42  $0.2 \text{ nm/min}$ , which gives the best homogeneity of the deposit. The deposition time was varied between 0.2 and  
43 1.6 min which corresponds to deposited thicknesses ( $\theta$ ) from 0.125ML to 6MLs.  
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48 The samples prepared in the above-mentioned way were thoroughly characterized by micro-Raman  
49 spectroscopy, performed using a Renishaw Invia Qotor equipped with a confocal optical microscope in back  
50 reflection geometry. A 532 nm excitation laser was employed with an excitation power of 0.5 mW and a 1800  
51 line per millimeter grating (spectral resolution  $2 \text{ cm}^{-1}$ ). The laser beam was focused onto the sample by a  $\times 100$   
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3 objective with a numerical aperture NA=0.85 and a spot size of 800 nm. All the Raman spectra are acquired  
4 with an acquisition time of 3 s. All the Raman analyses were carried out in air after air exposure of the samples.  
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7 Structural characterization of the samples before and after silicon deposition was investigated by STM  
8 measurements in UHV conditions using electrochemically etched tungsten tips. The UHV chamber is  
9 equipped with low energy electron diffraction (LEED), monochromatic XPS and a STM (Omicron). STM  
10 observations were carried out at room temperature using constant current mode with  $I_t = 0.3$  nA and  $V_t$   
11 between 0.2 and 2.0 V. They were performed on the samples as grown and after annealing in UHV at  
12 temperatures around 850°C to assess the stability of the deposit. A photon energy of 1486.6 eV (Al-K $\alpha$ ) for  
13 monochromatized XPS measurements was used for all samples. The photoelectrons are analyzed with an  
14 Omicron EA 125 energy analyzer with a 30eV pass energy. The quantification through XPS analysis of the  
15 Si/C ratio, estimated a Gr coverage of 1ML as detailed elsewhere.<sup>68</sup> AFM images were obtained in non-contact  
16 mode in air at room temperature (Park Systems) using standard silicon cantilevers. AFM and STM data were  
17 analyzed by WSxM<sup>94</sup> and ImageJ software. The XPS spectra were fitted using the CasaXPS software. All the  
18 XPS and STM analyses were carried out in a UHV chamber different from the MBE growth one. Therefore,  
19 all the samples experienced air exposure during the transfer.  
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## 30 SUPPORTING INFORMATION

31 The Supporting Information is available free of charge online.

32 The supporting information file gives more details on the morphology of the graphene surface after deposition  
33 of silicon for increasing coverages (from 0.125ML to 6ML). SEM, AFM and STM images are provided  
34 together with the deconvolution of XPS Si2p peak. The rough morphology of silicon deposited on uncleaned  
35 graphene substrate is also displayed. The figures provided are:  
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38 S-1. Large scale SEM and AFM images of the (6x6)Gr substrate

39 S-2. SEM observations for silicon coverages between 0.125ML and 6ML

40 S-3. AFM additional images for silicon coverages between 0.125ML and 6ML

41 S-4. STM images after deposition of 0.5ML silicon on graphene

42 S-5. Deconvolution of XPS Si2p peaks obtained after Si deposition on Gr/SiC with coverages varying between  
43 0.125 and 6ML

44 S-6. AFM images of the silicon surface after deposition on uncleaned Gr substrate  
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41 **Author Contributions**

42  
43 The manuscript was written through contributions of all authors. All authors have given approval to the final  
44 version of the manuscript. All the authors contributed equally.  
45  
46

47 **Funding Sources**

48  
49 P.C. and M. D.C., would like to acknowledge the European Community for the HORIZON2020 MSC-RISE  
50 Project DiSeTCom (GA 823728).  
51  
52

53 **Acknowledgments**

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3 The authors acknowledge the Nanotecmat platform. H.V. would like to acknowledge the HPC centers of  
4  
5  
6 IDRIS (Grant A0100900642 ) and CERMM for computational resources.  
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