

Silicene Phases on Ag(111)

Guy Le Lay

Aix-Marseille University
CNRS, PIIM UMR 7345
F-13397 Marseille, France
guy.lelay@univ-amu.fr

Seymur Cahangirov, Lede Xian, Angel Rubio

Nano-Bio Spectroscopy group
Universidad del Pais Vasco and ETSF
E-20018 San Sebastian, Spain
angel.rubio@ehu.es

Abstract—Silicene, an atom-thin two-dimensional sheet of silicon atoms arranged in a honeycomb lattice, recently synthesized on Ag(111), has attracted considerable interest as a potential alternative to graphene. For single layer silicene, two main phases have been identified among a few possible ones. They correspond to differently buckled silicene sheets, in coincidence either with 4×4 or $\sqrt{13} \times \sqrt{13}R(13.9^\circ)$ silver (111) supercells. Instead, we demonstrate via surface crystallography considerations and Density Functional Theory calculations that a previously claimed, $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ Ag(111) superstructure cannot accommodate a true honeycomb silicon sheet.

Keywords—silicene; silver; silicon; superstructures;

I. INTRODUCTION

Research on two-dimensional (2D) materials is flourishing in nanoscience, boosted by the experimental discovery of graphene. Since the first artificial synthesis of silicene [1,2], graphene's silicon cousin, which does not exist in nature [3], on a silver (111) substrate [4,5] and on a zirconium diboride (0001) template [6], a huge interest concerns graphene-like materials, especially, synthetic elemental ones from the same column of the periodic table. In accord with the name silicene, they are coined germanene [2] and stanene [7] (also dubbed tinene [8]), when based on germanium or tin, respectively.

Germanene has just been fabricated on platinum (111) and gold (111) surfaces [9,10], while stanene/tinene is still awaiting for its artificial creation.

Work on silicene, this novel paradigmatic 2D material, has developed at a very high pace. Nevertheless, silicene is just in its infancy; hence it is no surprise that many questions remain open and that some issues are still controversial. Typically, identification of real silicene phases among potential candidates is not a trivial task; hence, wrong assignments have been made, creating damageable confusion.

After summarizing results on the two main silicene phases recently synthesized on silver (111), namely the 4×4 and the $\sqrt{13} \times \sqrt{13}$ ones we clarify the case of the debated " $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ silicene phase" on Ag(111) [11,12], which has been already severely questioned [13].

II. REAL SILICENE PHASES ON SILVER (111)

Upon in situ deposition of silicon in ultra-high vacuum onto the clean (111) surface of a silver single crystal held at

$\sim 220^\circ\text{C}$ one can form a highly ordered 4×4 superstructure [4], which can cover 95% of the crystal surface [14]. Scanning Tunneling Microscopy topographs reveal a unique "flower pattern", as shown in Fig. 1a, that was interpreted as an epitaxially aligned 3×3 reconstructed buckled silicene sheet in coincidence with a 4×4 Ag(111) supercell, thanks to the perfect match between three silicene basis vectors and four silver surface ones, the presence of a linear dispersion at the K point of the silicene Brillouin zone in Angle-Resolved Photoelectron Spectroscopy measurements (ARPES) and Density Functional Theory calculations in the Generalized Gradient Approximation (DFT-GGA). Accordingly, we name this silicene phase $3 \times 3 / 4 \times 4$. The flower pattern results from the puckered Si atoms sitting right on top of Ag atoms, giving a total corrugation of the silicene sheet of $\sim 0.07\text{ nm}$. Hence, the silicene sheet was *not directly visualized* as a honeycomb array, but instead, derived indirectly from its unique flower pattern appearance [4]. This was confirmed by other groups and has established incontrovertibly the synthesis of silicene on silver (111), as shown in Fig. 1 [4,5,14,15,16].

At a somewhat higher preparation temperature ($\sim 250^\circ\text{C}$) another atom-thin 2D phase can occupy large areas; it is very likely a $\sqrt{7} \times \sqrt{7}R(\pm 13.9^\circ)$ reconstructed buckled silicene phase in coincidence with $\sqrt{13} \times \sqrt{13}R(\pm 30^\circ)$ silver (111) supercells. The in-plane Si-Si distance in this $\sqrt{7} \times \sqrt{7} / \sqrt{13} \times \sqrt{13}$ phase is just slightly expanded and the nominal surface coverage ratio would be $14/13 = 1.08$, slightly lower than that of the archetype $3 \times 3 / 4 \times 4$ phase with reference coverage ratio $18/16 = 1.125$.

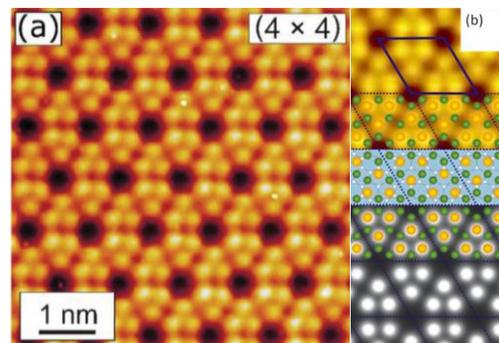


Fig. 1 (a) STM image of the $3 \times 3 / 4 \times 4$ silicene sheet on Ag(111); (b) STM image of the 4×4 phase taken at $U = 5\text{ mV}$; the size is $3.05 \times 2.63\text{ nm}^2$ and $I = 0.2\text{ nA}$. Below the STM image one sees an STM simulation from a previous calculation, based on the superposed ball model; adapted from refs 4, 15 and 16.

Symmetry imposes the existence of four domains, which have been recently observed in STM imaging (see Fig. 2) [17]. DFT-GGA calculations support the silicene assignment [18], although, at the moment, the effective presence of π bands, as detected in ARPES for the $3 \times 3 / 4 \times 4$ phase [19,20], has, to the best of our knowledge, not yet been proved experimentally.

III. THE CLAIMED HIGHLY PERFECT “ $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ SILICENE PHASE”

In a short letter showing only STM topographs [11], Lalme et al., announced in 2010, the first synthesis, strictly below 250°C , of a highly perfect silicene sheet having not even a single defect in a large scale topograph (see Fig. 1 in ref. 11); this sheet was mentioned to cover the whole scanned area (several hundred nm^2). It *displayed directly* a remarkable honeycomb arrangement with a very small buckling of just 0.02 nm. The authors stressed that this arrangement corresponded to an in-plane Si-Si distance $d_{\text{Si-Si}} \sim 0.19$ nm, although the profile pointed clearly, instead, to a much smaller value of 0.17 nm. The honeycomb array was claimed to be in coincidence with a $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ silver (111) supercell. However, such a superstructure was not at all visible in the STM image and no diffraction pattern was provided to support this claim, although the authors mentioned Low Energy Electron Diffraction observations (as well as Auger Electron Spectroscopy measurements, also not shown). A top view ball model of a “silicene phase” in coincidence with a $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ silver (111) supercell was assumed (see Fig. 3 in ref. 11), but not supported by any calculation.

Other experimental groups rapidly noticed many inconsistencies in this paper (see, e.g., ref. 5), while we could demonstrate that the make-believe “ $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ silicene phase” was just the result of a contrast inverted image of the bare Ag(111) surface [13]. This explains why neither a LEED pattern nor a Auger spectrum was presented in ref. 11 and why the “ $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ silicene phase” was never reproduced, even by its own promoters.

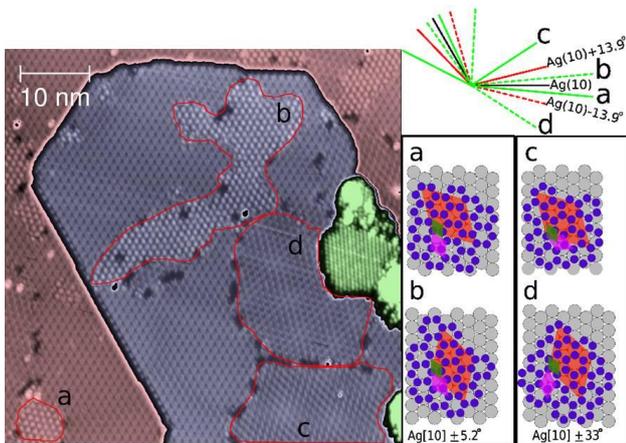


Fig. 2 STM image showing the four expected $\sqrt{7} \times \sqrt{7} / \sqrt{13} \times \sqrt{13}$ silicene domains in addition to the prototypical $3 \times 3 / 4 \times 4$ silicene structure on Ag(111). Adapted from ref. 17.

From basic surface crystallographic considerations, if existing, a $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ silver (111) super cell could accommodate a low buckled $\sqrt{7} \times \sqrt{7}R(\pm 13.9^\circ)$ reconstructed silicene sheet (symmetry imposing two rotational domains) with a coverage ratio of $14/12 = 1.167$ and an in-plane Si-Si distance of 0.218 nm, to be compared with the corresponding lower values of 1.125 and 1.08 respectively, for the real $3 \times 3/4 \times 4$ and $\sqrt{7} \times \sqrt{7} / \sqrt{13} \times \sqrt{13}$ silicene phases described in the previous section. Several DFT calculations (see, e.g., ref. 18) support the possible existence of such a phase. However, only experimental observations of highly defective “ $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ ” superstructures obtained at high temperatures ($\sim 300^\circ\text{C}$) have been reported [21]. The notation within “ ” is adopted here to indicate that this is not a real $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ superstructure, as already underlined by Moras et al. [22].

We believe that the non-existence of a real silicene $\sqrt{7} \times \sqrt{7} / 2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ phase can be simply explained by the higher Si atom number density it would necessitate, compared to the value for the prototypical $3 \times 3 / 4 \times 4$ silicene phase, and the associated, energetically unfavorable, in-plane compressive strain [18].

THE GHOST $2\sqrt{3} \times 2\sqrt{3}$ PHASE

We have noted in the previous section that the proponents of the highly perfect $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ phase [11,12] have emphasized an in-plane Si-Si distance of about 0.19 nm. As a matter of fact, such a distance would exquisitely match with a $3 \times 3 / 2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ phase, a point remained unnoticed. This is a case that we have theoretically examined, since no calculation for such a possible arrangement has appeared until now. Indeed, in principle, such a strained phase, although energetically unfavorable for free standing silicene [2], could be possibly stabilized by the interaction with the Ag(111) substrate (see Fig. 3).

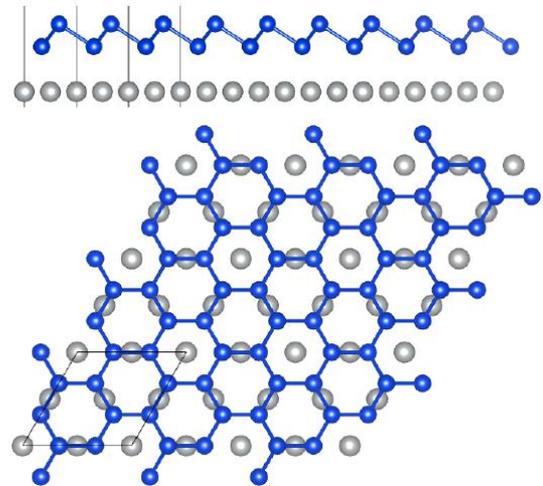


Fig. 3 Top and side view of the starting model of the hypothetical $3 \times 3 / 2\sqrt{3} \times 2\sqrt{3}$ phase for the DFT calculations. Blue balls: Si atoms, grey balls: Ag atoms.

We have thus performed first principles calculations based on DFT as implemented in the VASP code [23]. The exchange-correlation potentials are treated with the GGA-PBE approximation [24]. The atom ionic cores are modeled with the Projected-Augmented Wave pseudo-potential method [25]. As the $3 \times 3 / 2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ configuration would correspond, *de facto*, by symmetry, to a $\sqrt{3}$ silicene superstructure of a primitive $\sqrt{3} \times \sqrt{3}R(30^\circ) / 2 \times 2$ arrangement, we performed the calculations in these conditions, starting from a hypothetical buckled silicene layer. All atom positions were relaxed, except the Ag ones of the 3 bottom layers, which were fixed at the experimental in-plane lattice constant of 0.289 nm. We used a vacuum distance larger than 1 nm and sampled the Brillouin zone with $5 \times 5 \times 1$ k points. However, after relaxation, the layer completely collapsed, falling apart into broken pieces, as shown in Fig. 4. This demonstrates the inherent instability of the hypothetical $3 \times 3 / 2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ silicene configuration. Furthermore, it definitively confirms that a silicene sheet can not experience an in-plane compressive strain on a silver (111) template. Hence, we can assess at this stage that no epitaxial silicene phase with an in-plane Si-Si distance of about ~ 0.19 nm can be formed on a silver (111) substrate. We note in addition, that a plausible $\sqrt{7} \times \sqrt{7} / 2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ phase with, instead, $d_{\text{Si-Si}} = 0.218$ nm, appears, just as a dying or ghost phase, thereby adding insult to injury as expressed by Acun et al. [26].

IV. SUMMARY

Confusion has been maintained in the literature about a “ $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ silicene phase” grown on a silver (111) template. Initially claimed to be formed below 250° C in a highly perfect, nearly flat, arrangement with a small in-plane Si-Si distance of $d_{\text{Si-Si}} \sim 0.19$ nm, but geometrically modeled, instead, with a larger $d_{\text{Si-Si}}$ value ~ 0.218 nm [11], it was also shown, with a highly defective appearance, while grown at 300° C, without any clear distinction between the two very different cases [12].

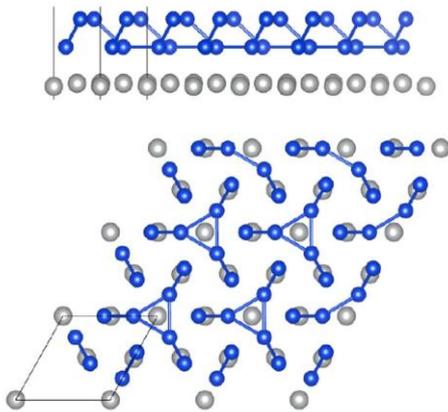


Fig.4 Relaxation result showing the instability of the hypothetical $3 \times 3 / 2\sqrt{3} \times 2\sqrt{3}$ phase.

We have definitively clarified the situation upon close examination of the surface/interface crystallographic structures and upon performing timely DFT calculations. Never reproduced, even by its promoters, the claimed perfect $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ silicene phase is just a delusive phase, while, adding insult to injury, the defective “ $2\sqrt{3} \times 2\sqrt{3}R(30^\circ)$ silicene phase” itself, which does not really exist as such, is just considered as a ghost phase.

Acknowledgments

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