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The Potentially Crucial Role of Quasi-Particle Interferences for the Growth of Silicene on Graphite

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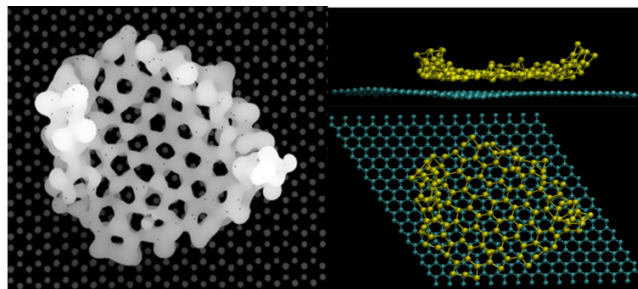
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Keywords: silicene; HOPG; self-assembly; *ab initio* calculations; scanning tunneling microscopy; quasi-particle interferences; surface charge modulations.

ABSTRACT

A comprehensive picture of the initial stages of silicene growth on graphite is drawn. Evidence is shown that quasiparticle interferences play a crucial role in the formation of the observed silicene configurations. We propose, on one hand, that the charge modulations caused by those quantum interferences serve as templates and guide the incoming Si atoms to self-assemble to the unique $(\sqrt{3}\times\sqrt{3})R30^\circ$ honeycomb atomic arrangement. On the other hand, their limited extension limits the growth to about 150 Si atoms under our present deposition conditions. The here proposed electrostatic interaction finally explains the unexpected stability of the observed silicene islands over time and with temperature. Despite the robust guiding nature of those quantum interferences during the early growth phase, we demonstrate that the window of experimental conditions for silicene growth is quite narrow, making it an extremely challenging experimental task. Finally, it is shown that the experimentally observed three-dimensional silicon clusters might very well be the simple result of the end of the silicene growth resulting from the limited extent of the quasiparticle interferences.

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Charge modulations caused by quantum interferences (QI) on graphene guide Si atoms to self-assemble to the unique $(\sqrt{3}\times\sqrt{3})R30^\circ$ honeycomb atomic arrangement. The limited extend of those QI leads to the experimentally observed transition from 2D to 3D growth at the outskirts of the silicene islands.

INTRODUCTION

Since the Nobel-prize winning discovery of graphene, much research has been dedicated to alternative two-dimensional (2D) materials that might overcome the principle drawback of graphene of being gapless [1]. One of these materials is the silicon analogue, named silicene. Recently, it had been proposed to grow silicene on chemically inert graphite substrates instead of metal substrates, to avoid the possible formation of alloy materials, which is a necessary condition to preserve the Dirac properties as the ones known for graphene [2].

The ultimate proof that the STM measurements (*i.e.* images and associated height profiles) presented in Ref. [2] originate, indeed, from Si atoms and not from possible charge modulations [3-5] is given by the Raman measurements reported in Ref. [6]. As detailed there, the studied samples display a patchwork of nano-sized regions with a $(\sqrt{3}\times\sqrt{3})R30^\circ$ honeycomb superstructure. The corresponding Raman analysis reveals the presence of a resonance located at 542.5 cm^{-1} . This position of the Raman peak perfectly fits the atomic vibration of Si atoms in a $(\sqrt{3}\times\sqrt{3})R30^\circ$ honeycomb silicene nano island deposited on HOPG, found by first-principles calculations. It cannot be explained by charge modulations. Those Raman spectra have actually become the identifying “fingerprint” for our silicene nanosheets [6]. The formation of genuine silicene nano islands is then strongly supported by a large body of evidence not restricted to STM measurements and *ab initio* calculations, but it also finds confirmation by the direct measurement of the vibrational movement of Si atoms forming finite silicene nano islands.

We would like to stress that the results of our Raman measurements have very recently been confirmed by Yue *et al.* showing a Raman frequency close to ours at 550 cm^{-1} for their experimentally observed silicene-like islands [7]. Those authors also confirm the apparent stability of their silicene nanostructures toward oxidation [7], as reported in our previous work [6].

For the present work, we have performed additional experiments and *ab initio* simulations that provide new insight in the process of growing silicene on graphite that might not only be thought-provoking to the materials nanoscience community, but that might also rapidly open possibilities for the controlled growth of nanostructures on an atomic scale.

1. METHODS

1.1 Experimental:

A HOPG (from GE Advanced Ceramics, USA, 12 mm x 12 mm x 1 mm) sample was used as a substrate. A fresh surface of graphite was obtained by peeling the HOPG substrate with Scotch™ tape in a nitrogen atmosphere and was then transferred into an ultra-high vacuum (UHV) chamber. High-purity silicon (Sil'tronix ST, $\rho=1-10 \Omega \times \text{cm}$) was evaporated from a tungsten basket-shaped crucible located at 200 mm from the substrate. The deposition was done in UHV conditions (base pressure low 10^{-10} Torr) and at a constant rate of 0.01 nm/min (0.04 ML/min), monitored by an Inficon quartz balance (properly calibrated for the Si density and carefully positioned close to the sample holder). Deposition was carried out keeping the substrate at room temperature. Samples were studied *in situ* at room temperature by scanning tunneling microscopy (STM) using an Omicron-STM system with electrochemically etched tungsten tips. The STM was calibrated by acquiring atomically resolved images of the bare HOPG. All images were acquired in the constant mode and were unfiltered apart from the rigid plane subtraction.

1.2 Computational:

Ab initio calculations were performed by using density functional theory (DFT) within the Generalized Gradient Approximation (GGA) including van der Waals corrections as implemented in the Vienna *ab-initio* Simulation Package (VASP) [8,9]. The Perdew-Burke-Ernzerhof (PBE) [10] with van der Waals-D2 functional [11] was used to describe the exchange-correlation

interaction. The core electrons were described by the projected augmented wave (PAW) method [12]. The plane-wave basis set was restricted to a cut-off energy of 400 eV. The HOPG surface was modeled by a four-layer slab with 56 carbon atoms per layer in an ABAB stacking of graphene within periodic boundary conditions, keeping the bottom two layers fixed. The vacuum region is as thick as 2.0 nm. The entire system; silicene on top of graphite, was fully relaxed by a conjugate gradient method until the forces acting on each atom were less than 0.1 eV/nm. The convergence criterion of total energy for self-consistent field calculations was chosen to be 10^{-4} eV. We have used $3 \times 3 \times 1$, and $9 \times 9 \times 1$ k-point meshes including the gamma point in order to sample the supercells with 30° and 10° rotation angles between the two hexagonal patterns, respectively. *Ab initio* molecular dynamics simulations within the NVT ensemble [13], using the Nose-Hoover thermostat [14] for temperature control, were performed using VASP. The time-step for all AIMD simulations was 1.0 fs.

2. RESULTS AND DISCUSSION

First of all, we fully agree with the findings of Cai *et al.* [15] that their proposed $\text{Si}\sqrt{21}/\text{Gr}2\sqrt{13}$ and $\text{Si}4/\text{Gr}\sqrt{39}$ configurations are energetically more favorable than the $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure observed in our experiments. However, we would like to remind the reader here that the calculations by Cai *et al.* are based on the assumption of an infinite silicene/graphene system and that our present experimental observations are limited to nano islands whose size never exceeds about 150 Si atoms (*i.e.* an area of about 3 nm x 3 nm); *i.e.*, we have to take into consideration the very early stages of the silicene growth on graphite. For this initial phase of the silicene growth, the van der Waals (vdW) interaction between Si atoms and the graphene substrate is of crucial importance. This interaction is that which is expected to guide the silicon atoms to specific configurations and that defines a plane above the graphite surface in which the impinging

Si atoms can self-assemble. Without this vdW interaction, most incoming Si atoms would simply form covalent bonds with graphite and serve as seeds for 3D silicon cluster growth by attracting and reacting with other Si atoms impinging on the graphite surface.

In the following, we have considered four different silicene configurations: the two most stable ones predicted by Cai *et al.*; *i.e.* the $\text{Si}\sqrt{21}/\text{Gr}2\sqrt{13}$ and $\text{Si}_4/\text{Gr}\sqrt{39}$ configurations, and the $(\sqrt{3}\times\sqrt{3})$ configuration for two different rotation angles; 10° and 30° . Optimization of the corresponding infinite structures at zero Kelvin leads to the results summarized in Table 1. While the total binding energies E_b for the infinite systems clearly suggest that the structures predicted by Cai *et al.* should be more stable, the vdW interaction energies E_{disp} turn out to be more favorable for both $(\sqrt{3}\times\sqrt{3})$ configurations. Actually, the $(\sqrt{3}\times\sqrt{3})\text{R}10^\circ$ configuration even leads to a slightly stronger vdW interaction than the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ one; however, it suffers from nearly twice as much strain, which makes it less likely to become the dominant configuration. We argue that at the very beginning of the silicene island formation, the Si atoms cannot primarily be guided by the properties of the infinite system, but rather by the weak vdW forces that are already present at this early phase.

System	E_b [eV per atom]	E_{disp} [meV per atom]
$\text{Si}\sqrt{21}/\text{Gr}2\sqrt{13}$	-7,71	-94,45
$\text{Si}_4/\text{Gr}\sqrt{39}$	-7,70	-95,22
$(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$	-7,67	-97,01
$(\sqrt{3}\times\sqrt{3})\text{R}10^\circ$	-7,65	-98,56

Table 1: Total binding energies (E_b) and van der Waals dispersion energies (E_{disp}) for four different silicene configurations.

To support our line of thoughts, we have calculated the total binding energy E_b per Si atom for finite silicene islands of different sizes, ranging from 6 to 130 Si atoms, placed on top of a graphite substrate considering two of the above configurations: the $\text{Si}\sqrt{21}/\text{Gr}2\sqrt{13}$ and the $(\sqrt{3}\times\sqrt{3})R30^\circ$ configurations (see Fig. 1). The latter one is, indeed, slightly more stable for the very smallest islands; however, the $\text{Si}\sqrt{21}/\text{Gr}2\sqrt{13}$ structure suggested by Cai *et al.* clearly becomes dominant for island sizes above about 50 Si atoms.

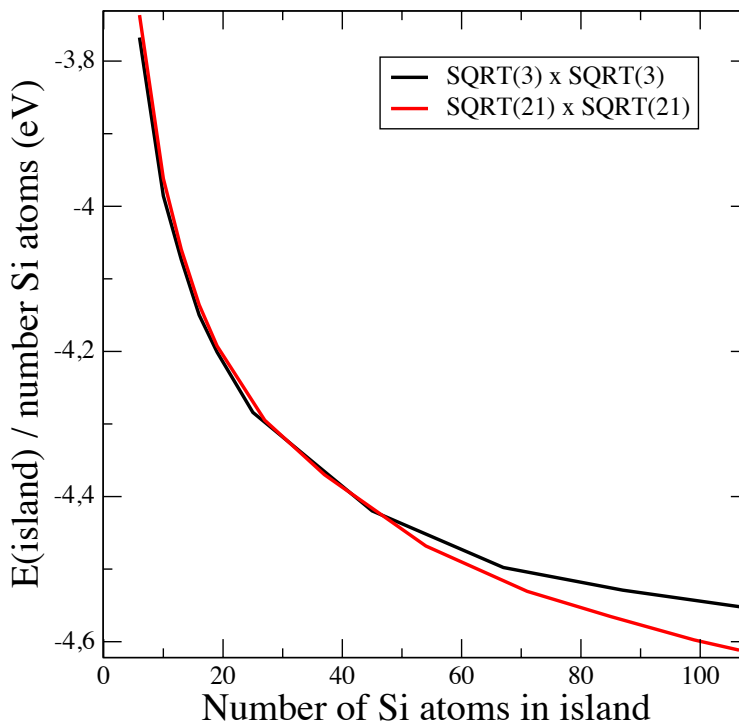


Figure 1: Total binding energies $E(\text{island})$ per Si atom of finite silicene islands for two different configurations: $(\sqrt{3}\times\sqrt{3})R30^\circ$ and $\text{Si}\sqrt{21}/\text{Gr}2\sqrt{13}$.

However, even with the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure being the most stable one for the smallest islands, the energy difference relative to all other configurations is so small, that we should have, indeed, observed a mixture of different configurations as suggested by Peng *et al.* and not only the

$(\sqrt{3}\times\sqrt{3})R30^\circ$ one at any realistic temperature. Despite all experimental efforts, however, it is only the $(\sqrt{3}\times\sqrt{3})R30^\circ$ configuration that always emerges with the HOPG substrate, whereas the expected variety of different reconstructions had been observed for the Si/Ag(111) system [16,17]. To elucidate this striking dissimilarity, we would like to recall the major difference between the two systems: in contrast to the Si/Ag(111) system, all interactions between silicene and HOPG are exclusively of the vdW type without any hybridization or covalent bond formation.

Quasi-particle interferences resulting from the interaction between normal and scattered electron waves are known for both HOPG/graphene systems [4,5] and metal substrates [18-20]. For all cases, however, the presently observed amplitude significantly exceeds the one measured on metal surfaces in early STM experiments by a factor of 25. Therefore, we tentatively propose here that the charge modulations resulting from the quantum interferences guide the incoming Si atoms to positions above the graphite substrate that correspond to a template given by those charges. For graphene nano ribbons, it has been shown that many different interference patterns are possible that depend on the precise nature of the ribbon edges [5]. For a HOPG substrate, however, it has been well-established that $(\sqrt{3}\times\sqrt{3})R30^\circ$ patterns should be dominant [3].

To support our working hypothesis, we would like to remind the reader that the interaction energy between a point charge and a neutral Si atom varies as $1/r^4$, with “r” being the distance in between [21]. We are here introducing the interaction between transient charges induced in the Si atoms and the permanent charges resulting from the quasiparticle interferences. In contrast, the energy for the vdW interaction between Si atoms and the HOPG substrate follows a $1/r^6$ law [21,22]. Qualitatively, the forces resulting from the surface charges are thus dominant for the guidance during the initial silicene island growth because they are acting over longer distances than the pure vdW forces between the substrate atoms and the Si atoms. As a direct consequence,

only silicene islands with a $(\sqrt{3}\times\sqrt{3})R30^\circ$ pattern as prescribed by the quantum interferences on a graphite substrate will be formed although other configurations might be more stable in the absence of quasi-particles.

Following our working hypothesis further, we can now also understand why we could never observe silicene islands exceeding a size corresponding to roughly 150 Si atoms. Our proposed growth mode should limit the size of silicene islands to the extension of the quantum interferences which we observed experimentally [4]. As previously reported [3], those quantum interferences are typically limited to about 3 to 4 nm. However, there is no fundamental reason for such a limit. In principle, larger areas of quantum interferences could be created if the energy loss to the substrate was minimized; *e.g.* by minimizing phonon-electron scattering at very low temperatures.

Nevertheless, even with nearly undamped infinite quantum interferences, there are still two beat frequency phenomena that have to be considered: the first one concerns the lattice constant mismatch between the one defined by the wavelength of intervalley scattering on graphite of $3*a/2$, with “*a*” being the length of the graphene lattice vector, which is roughly 0.37 nm [5] and the one of silicene islands of about 0.41 ± 0.02 nm [2,6]. With such a mismatch, a maximum de-phasing between the two honeycomb patterns should be expected after the growth of about 7 to 10 hexagons in each planar direction, which roughly corresponds to our experimental observations for the size of the largest silicene islands. There is, however, yet another mismatch that has to be considered, namely the one resulting from the difference between the wavelength of intervalley scattering ($3*a/2$) and the lattice periodicity ($\sqrt{3}*a$), with “*a*” being the length of the graphene lattice vector in both cases. Park *et al.* have actually given the experimental proof for such a mismatch in observing a beat pattern with a periodicity of 3 nm for pristine graphene [5]. Independent of the origin of the mismatch, the stabilizing electrostatic forces are the weakest at

the maximum mismatch explaining the faster out-of-plane movement of the edge atoms occurring in those regions leading to the end of the silicene growth when the flux of incoming Si atoms is too small. With a sufficiently high flux of Si atoms arriving at the island edges, however, we predict that those areas of smallest electrostatic stabilization can be overcome and larger silicene sheets can be grown.

At this maximum mismatch, or at the end of the HOPG areas for which quantum interferences are active, the stabilizing electrostatic forces from the charge modulations become minimal, permitting the island edge atoms to move more easily out of the growth plane. In fact, those Si edge atoms are the most prone to such a behavior because they are only two-times coordinated and do consequently not profit from the aromatic stabilization of the other honeycomb Si atoms. We like to point out that such a movement of the edge atoms is reversible if the flux of incoming Si atoms is high enough; *i.e.*, if the next Si atoms come in early enough, the edge atoms will move back in the 2D growth plane. However, if too much time has passed by; *e.g.* permitting a lateral movement that brings two Si atoms above each other, then the “*point of no return*” is reached and the Si atoms cannot return to their initial position. Instead, they become preferential seeds for 3D cluster growth at the outskirts of the silicene island. In this sense, we claim that the 3D clusters in contact with the silicene islands observed in our previous work are not necessarily the origin of the quantum interferences, but rather they are the result of the end of the silicene nano island growth. To support this idea, we like to remind that the necessary quantum interferences are well-known even for pristine graphite and graphene substrates without the need for any clusters [23,24].

A question that emerges at this point is whether the $(\sqrt{3}\times\sqrt{3})R30^\circ$ islands would reorganize or restructure to get closer to global minimum energy configurations, as the ones predicted by Cai. *et al.*, without the stabilizing effect of the quantum interferences. To explore this possibility, we cut

an island of about 150 Si atoms out of a perfect $(\sqrt{3}\times\sqrt{3})R30^\circ$ sheet and observed its evolution in the absence of newly incoming Si atoms. Rapidly, the under-coordinated island edge atoms reorganize themselves leading to an ill-defined island edge. We followed the development at room temperature and observed the beginning of a 3D structure growth at the island edge. Further incoming Si atoms would then lead to the formation of 3D clusters in direct contact with the nearly unchanged island center containing about 20 hexagons.

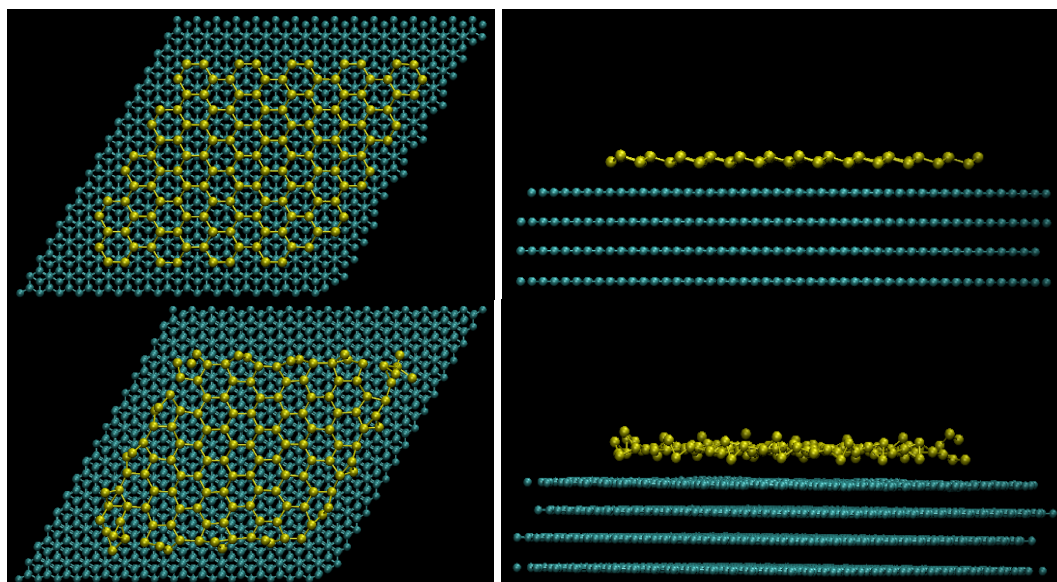


Figure 2: *Top and side view of the silicene island on HOPG at 38 K (top row) and 300 K (bottom row).*

To better illustrate this phase of the growth, we have displayed two snapshots of this typical silicene island at two temperatures (38 and 300 K) (see Fig. 2). As can easily be seen from the snapshot taken of the island at 300 K, only the Si edge atoms move, whereas the center honeycomb pattern remains perfectly preserved. However, we have to admit that our present AIMD simulations of the silicene island on a four-layer HOPG system are limited to about 1 ps. In order to have a qualitative idea of what could be expected at realistic experimental conditions, we temporarily replaced the HOPG substrate by a freestanding graphene layer for two reasons: first,

the simulation advances significantly faster due to the considerably smaller number of atoms and second, the process becomes much less conservative due to the thermal activation caused by the large amplitude, wavelike motion of the freestanding graphene substrate. The resulting amplitude actually becomes much more important than that for the four-layer HOPG case, for which the thermal motion is quite negligible for the investigated temperatures because the lowest layers always remained fixed [2]. It actually considerably exceeds even the largest known ripple and moiré structures for monolayer graphene on a metal surface [25]. For this large-amplitude freestanding graphene substrate, the silicene island exhibits such a high flexibility that it follows the movement of the graphene substrate without any problems. Needless to say, that we do not expect any quantitative information from such an over-simplified, unrealistic model. However, we can see qualitatively that the out-of-plane position of the edge atoms leads to the formation of 3D clusters that grow in size with further arriving Si atoms at the island edges. In Fig. 3, we noticeably remark the presence of two Si clusters that are connected by a silicene island exactly as it has been observed experimentally (see Fig. 4).

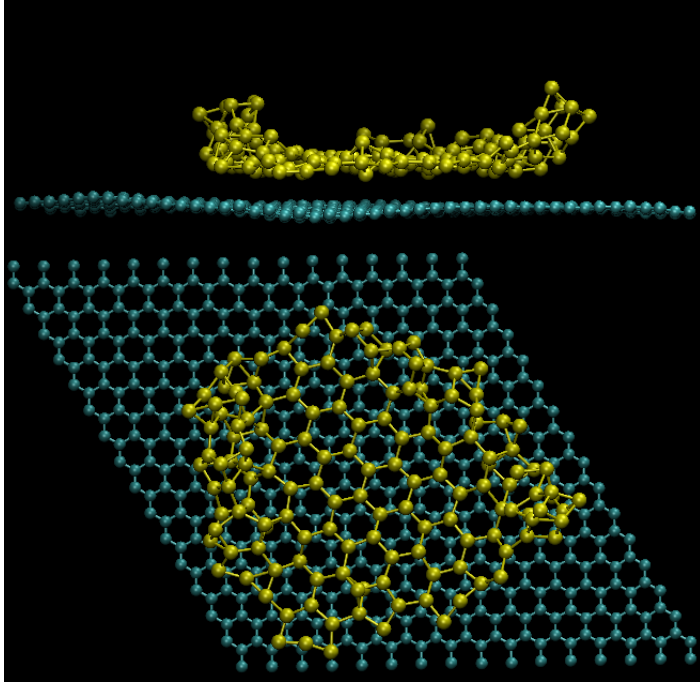


Figure 3: Side and top views of the silicene island after 6 ps at 350 K on top of an infinite freestanding graphene layer. Without the stabilizing effect of the quantum interferences and with a too low flux of incoming Si atoms, the Si island edge atoms move out of the 2D plane giving birth to 3D clusters at the outskirts of the silicene island as previously observed experimentally (see Fig. 4).

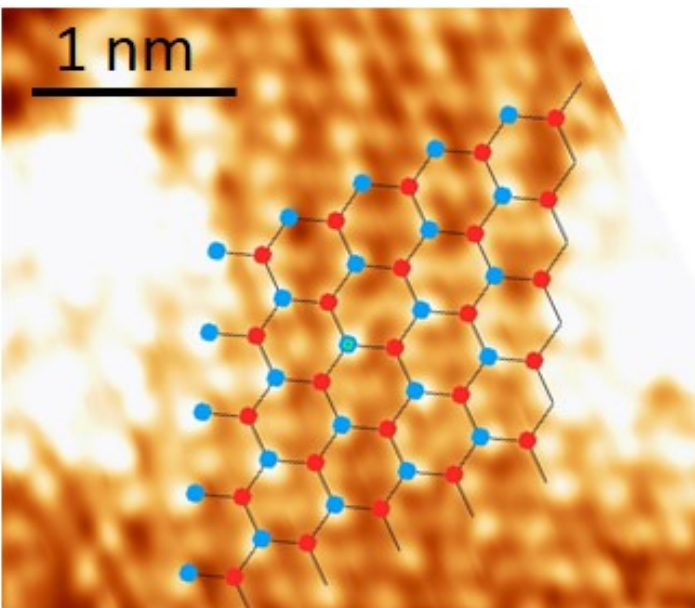
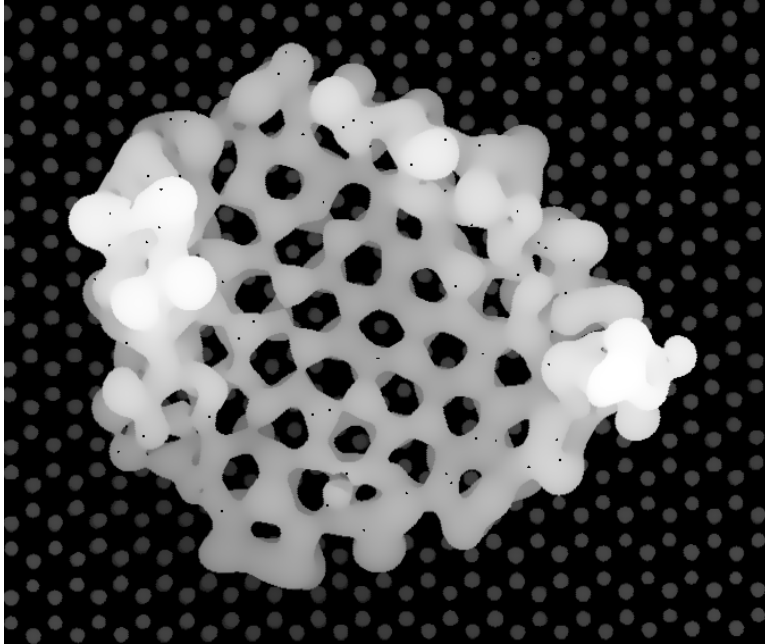


Figure 4: (above) *Simulation of the STM image resulting from the predicted island structure as shown in the previous figure;* (below) *experimental STM image of two silicon clusters that formed at the outskirts of a silicene island (see Fig. 3) as shown in Ref. [2].*

In the absence of stabilizing quantum interferences, we observe, in addition, a collective rotation of the island of nearly 30° toward a configuration that does bear some resemblance with the $Si\sqrt{21}/Gr2\sqrt{13}$ configuration predicted by Cai *et al.* after about 5 ps at 450 K (see Fig. 5) in our

simulations. Under this extreme thermal condition, however, the island rotation is not smooth; *i.e.*, not all parts of the island rotate at the same time leading to extensive strain in the island and breaking of hexagon bonds causing the loss of aromatic stabilization first, due to re-hybridization from aromatic to sp^2 and then, to the formation of sp^3 bonds which, again, become seeds for 3D cluster formation and, thus, the end of the 2D silicene growth. Qualitatively, we can further conclude without any doubt from our AIMD simulations that the out-of-the-2D-plane displacement of the island edge Si atoms happens much faster than any possible island rearrangement to a more stable configuration at any realistic temperature. Experimentally, however, we do not see any such configuration transition which might be due to several reasons; first, the experimental conditions might be much milder than the ones in our too violent freestanding graphene model; or second, the possible rotation might have destroyed most of the concerned island; or third, it could be that at the end of the quantum interferences, the resulting islands are already large enough that the movement of the Si edge atoms might be completely negligible. Another reason could be that the charge modulations of the quantum interferences play a paramount role in stabilizing the silicene islands leading also to their astonishing thermal stability on the experimental time scale, which is not accessible with our present AIMD simulations. For this latter possibility, however, more quantitative information concerning the quantum interferences is needed to account for their precise action appropriately and should be an exciting subject of further research.

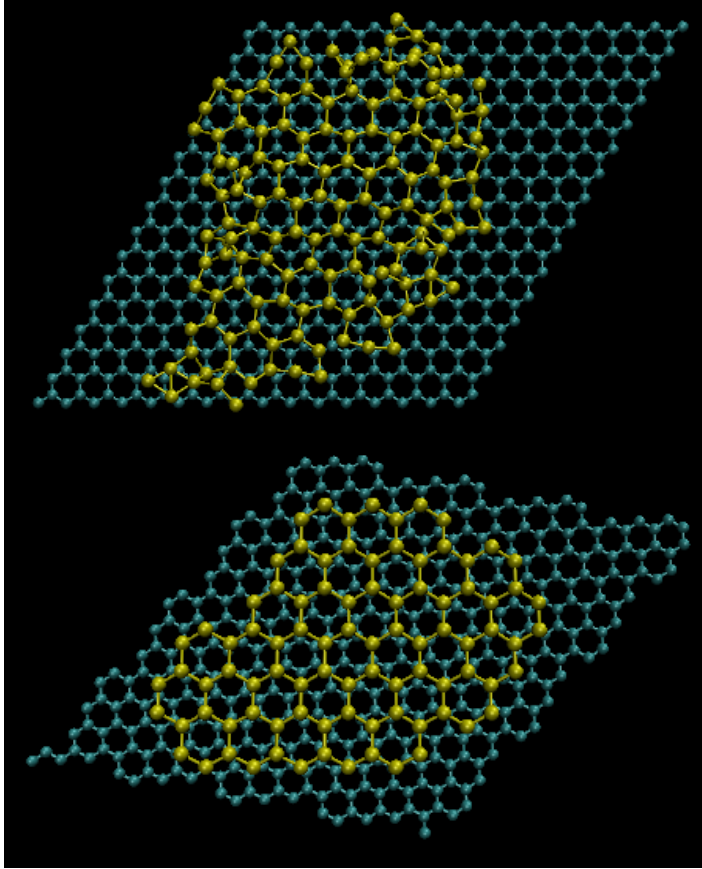


Figure 5: Comparison between a $(\sqrt{3}\times\sqrt{3})R30^\circ$ island after its spontaneous rotation at 450 K using a freestanding graphene substrate (above) and the $\text{Si}\sqrt{21}/\text{Gr}2\sqrt{13}$ configuration as predicted by Cai et al. at zero Kelvin (below).

To assure continuous silicene growth, the incoming Si atoms have to arrive at the growing island with such a high flux that the growth takes place at a faster rate than the possible reconstruction of the otherwise under-coordinated edge silicon atoms. Elsewise, the resulting non-hexagonal edge patterns will favor the growth of 3D structures due to their lack of aromatic in-plane stabilization. Consequently, 3D clusters may form at the edge of our silicene sheets manifesting the end of the silicene growth process. As the size of the growing island increases, we need more and more Si atoms arriving at the edges. Assuming a homogeneous surface diffusion

and circular islands, enough Si atoms should be supplied as the cross section for Si atom impact also increases with the radius of the island. However, the probability that an incoming Si atom might strike the island directly from above instead of arriving by surface diffusion from the sides increases with the square of the radius. As a consequence, the growing island will get at least partially destroyed beyond a certain size with a sufficiently high flux. As can readily be seen from our AIMD simulations of such a process, the impinging Si atom will not diffuse on the island toward the edge to participate in the on-going silicene growth, but they will simply form covalent bonds with sp^3 hybridization close to the impact area. In this manner, the 2D nature of the island will be jeopardized and further incoming Si atoms will again lead to a transformation to a 3D cluster.

Finding the optimal incoming flux is, therefore, a very delicate experimental challenge. In our AIMD simulations of a typical island with a roughly circular shape and a circumference of about 11 nm, for instance, we find about 36 Si edge atoms that are only two-times coordinated. As shown in Fig. 3, most of those Si atoms reversibly move out of the 2D growth plane within 6 ps at room temperature. Therefore, to assure a continuous growth, we need a new Si atom arriving by surface diffusion on each of those 36 Si edge atoms within an interval of about 6 ps to have those atoms return into the growth plane. If after the initial growth of very small silicene islands, the incident flux of incoming Si atoms is stopped or is too low, the islands will rapidly transform into 3D clusters as shown in Fig. 6 and as has been observed by Peng *et al.* In our AIMD simulations, we have used the highly flexible freestanding graphene substrate model, as described above, to observe this process on a time scale of 10 ps.

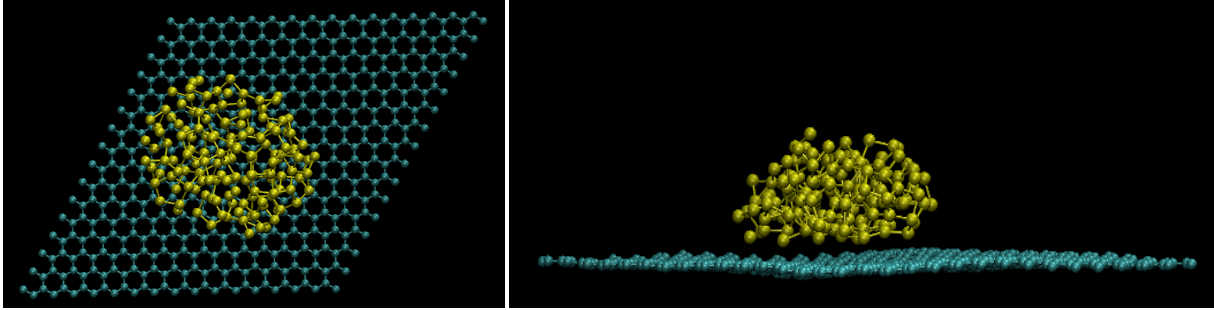


Figure 6: As observed by Peng et al. [3], 3D silicon clusters are formed if the flux of incoming Si atoms is too small.

For the ideal growth of silicene islands, we can conclude, on one hand, that the incoming flux of Si atoms should be small enough to assume that the direct impact of Si atoms onto the growing silicene island is negligible, because such impacts lead to the instantaneous formation of stable dumb-bell structures, either above or below the silicene island, and cause the formation of sp^3 bonded Si atoms on top of it. On the other hand, the flux of Si atoms arriving at the island edges via surface diffusion has to be high enough to assure that the edge silicene island atoms do not have time to form sp^3 binding moving them above or below the 2D plane and subsequently serving as seeds for 3D cluster formation, which also signals the end of the silicene growth and the beginning of the 2D/3D transition.

To avoid the impact of Si atoms onto the growing silicene island, we would finally like to suggest that the growth of very large silicene sheets might only become possible underneath a protective graphene sheet that excludes the arrival of Si atoms from above and limits the growth to atoms arriving at the island edges via surface diffusion between a non-reactive substrate and a covering graphene layer with some defects. An alternative for such an intercalation growth could be the use of hexagonal Boron Nitride (h-BN) as a protective cover layer. Some authors suggest that H-atoms have a higher chance to penetrate through a defect-free h-BN layer than through

graphene, while heavier atoms are more efficiently blocked [26]. However, the realization of h-BN with a well-controlled and appropriate defect density still presents a considerable experimental challenge; *i.e.*, there should be enough defects to permit a large number of Si atoms to get into the intercalation space but with an average distance between defects that is larger than the desired size of the silicene islands.

3. CONCLUSIONS

In conclusion, the present study illustrates how delicate it is to find suitable conditions for silicene growth on an inert graphite substrate. In our quest for a deeper understanding of the early phases of silicene growth on HOPG, we here propose the tentative hypothesis that the initial growth phase might be guided by charge modulations resulting from quantum interferences. Such a strong proposition, however, still requires much more exploration, but it already explains the ensemble of the existing experimental data; *e.g.* only the $(\sqrt{3}\times\sqrt{3})R30^\circ$ configuration is experimentally observed although other patterns should be energetically more favorable without quantum interferences, the silicene islands never grow larger than the extend of the quantum interferences, and the corresponding islands are unexpectedly stable with time and temperature. Therefore, our hypothesis might ultimately open up completely new avenues for the controlled synthesis of nanostructures once the related engineering of charge modulation patterns will be mastered.

AUTHOR INFORMATION

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Author Contributions

The manuscript results from an intensive collaboration between experimentalists and theoreticians; the theory has been proposed and all simulations have been performed by FJ, CL, and HV. All authors have given approval to the final version of the manuscript.

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