Physics and chemistry of silicene nano-ribbons

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ABSTRACT

We review our recent discovery of silicene in the form of silicon nano-ribbons epitaxially grown on silver (1 1 0) or (1 0 0) surfaces, which paves the way for the growth of graphene-like sheets. We further draw some perspectives for this unique novel material upon mild hydrogenation.

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1. Introduction

Graphene, a one-atom thick single sheet of graphite where sp^2-bonded carbon atoms are arranged in a honeycomb lattice, is presently one of the most studied novel material in nanoscience and nanotechnology, mainly since a method to produce free standing flakes by mechanical exfoliation has been devised in 2004 [1]. However, albeit generally denominated as a graphite-like monolayer, graphene has been known for at least 40 years in the adsorbed form on metal surfaces [2] and for more than 10 years on the 6H-SiC(0 0 0 1) one [3]. The graphene *boom* stems from its striking properties. Due to the peculiar electronic structure of the π and π^* bands, which form a so-called Dirac cone at the Fermi energy at the Brillouin zone corner (K points), its charge carriers behave like massless relativistic particles. High carrier mobility independent of concentration and temperature typically permits to envision high-speed electronic devices based on ballistic transport at room temperature [4].

However, graphene cannot fit easily into the silicon-based electronics industry. Hence, "graphenium" microprocessors are unlikely to appear in the near future as it is hard to see chip makers re-tooling to use carbon instead of silicon. As a consequence, substantial theoretical efforts have recently focused on the hypothetical silicon analogue, i.e., graphene-like silicon, coined "silicene" [5].

π bonding and the associated planar sp^2-type coordination is not frequent for silicon molecules; to the best of our knowledge, silicon benzene (hexasilabenzene) has not yet been synthesized [6,7]. Yet, theoretical models of silicon nanotubes (SiNTs) have been built on a benzoid structure (Si hexagons in sp^2 hybridization) [8–10], while experimental evidence of some sp^2 bonding in single wall SiNTs has been presented [11]. Theoretical calculations on silicene either in a flat [5,9,12] or a low-buckled configuration [13,14] generally concur on the fact that the honeycomb structure should be stable, with an electronic structure similar to that graphene. In other words, the π and π^* bands also cross at the K points with linear dispersions, which attributes a massless Dirac fermion character to the charge carriers (see Fig. 1).

Still, the mere existence of silicene has been recently questioned [15], although the soft synthesis of single-crystal silicon monolayer sheets (with evidence of a hexagonal structure) has been achieved (see Fig. 2) [16]. This shows that ultimate sheets of silicon can be obtained in way that can be compared with obtaining monolayer graphene upon graphite pealing.

Besides, several reconstructions, in the form of self-aligned stripes, induced by adsorption of metals onto the clean Si(1 1 1)7 × 7 surface, typically the Si(1 1 1)5 × 2-Au one [17],

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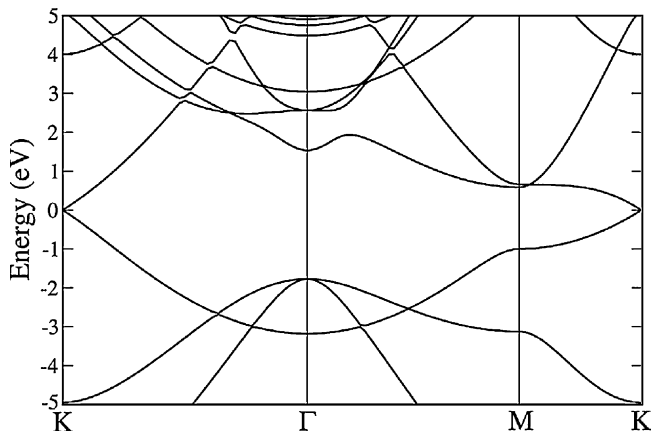E-mail address: lelay@cinam.univ-mrs.fr (G. Le Lay).

Fig. 1. The band structure of silicene calculated with DFT [12]. The Fermi level is set at 0 eV.

are associated with a typical structure involving "suspended" silicon nano-ribbons (SiNRs) in a honeycomb arrangement (see Fig. 3), with striking one-dimensional electronic responses [18].

In the following we review our recent results on silicon adsorption on silver substrates. Silver is totally unreactive with silicon and favors catalytically its growth in a graphene-like arrangement.

2. Evidence of epitaxial growth of silicene in the form of nano-ribbons

2.1. On the Ag(1 1 0) surface

As mentioned above, it has been known for long that several single crystalline metal surfaces catalyse the epitaxial growth of graphene sheets either by segregation of carbon from the bulk or upon Chemical Vapor Deposition, e.g., decomposition of ethylene (see [2] and references therein). Possibly, we could anticipate that a judicious choice of an unreactive metal substrate, such as silver, could favor the growth of ultra-thin novel silicon structures. Nevertheless, when we first deposited Si in situ under ultra high vacuum onto the clean Ag(1 1 0) surface, it was a surprise to discover a striking arrangement of massively parallel SiNRs, perfectly aligned along the [$\bar{1}$10] directions of the surface, as shown in Fig. 4 [19].

We have carried out a detailed investigation of the physical and chemical properties of these SiNRs by a synergetic combination of STM/STS, high-resolution synchrotron radiation photoelectron spectroscopy [19,20] and Density Functional Theory calculations. These novel silicon nanostructures display a x2 periodicity along their edges. They possess a "magic" width of just 1.6 nm, show a surprising transverse symmetry breaking and a substrate mediated cross-talk, which induces their chiral organization in magnetic-like domains [20]. Their spectroscopic signatures are unique: strong metallicity, quantized electronic states, narrowest
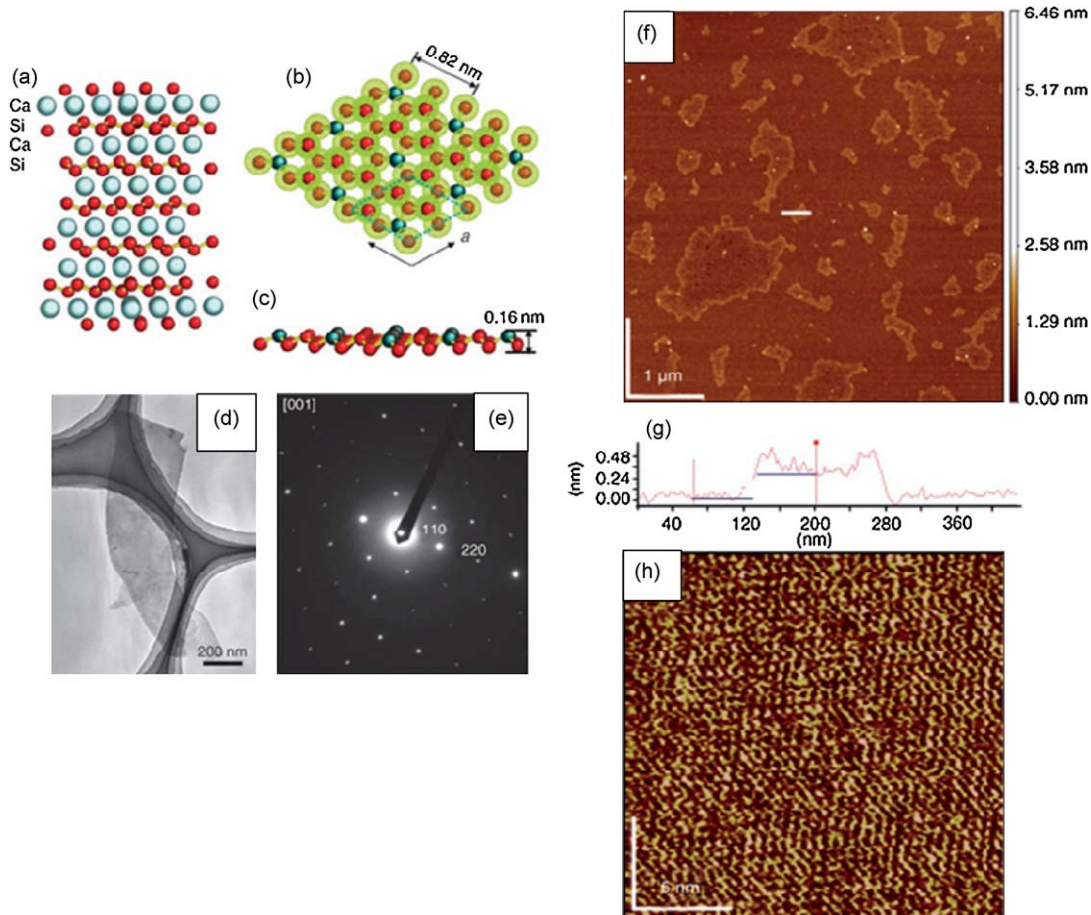

Fig. 2. (a) Structural model of CaSi$_2$. (b) Top view of a Mg-doped silicon sheet capped with oxygen. (c) Side view of the core of the silicon sheet; large yellow-green circles: O, small red: Si and green: Mg ones represent the Si(1 1 1) plane in the layer below. (d) TEM image of the sheet. (f) Its ED pattern recorded along the perpendicular [0 0 1] zone axis. (g) Noncontact mode AFM image of the silicon sheets. (h) Its line profile along the white line in (f). (h) Atomically resolved AFM image. Adapted from Figs. 1–3 of Ref. [16]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
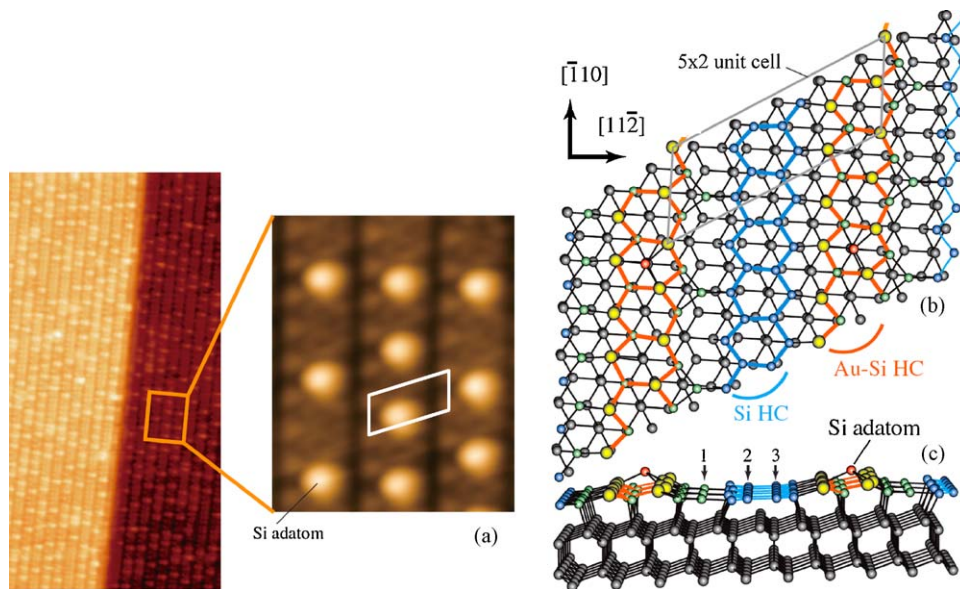
Fig. 3. (a) 30 nm × 16.5 nm STM image (Vs = 1.5 V) of the Si(1 1 1)5 × 2-Au surface showing a step as well as the array of 1D atomic wires running along the [Ī10] direction and a zoom-in (2.2 nm × 1.8 nm, Vs = 1.0 V) showing clearly the topographic atomic features; (b) and (c) show the top and side view of the structural model proposed by Erwin [35]. Large and small balls are Au and Si atoms, respectively. Adapted from Fig. 1 of Liu et al. [18].
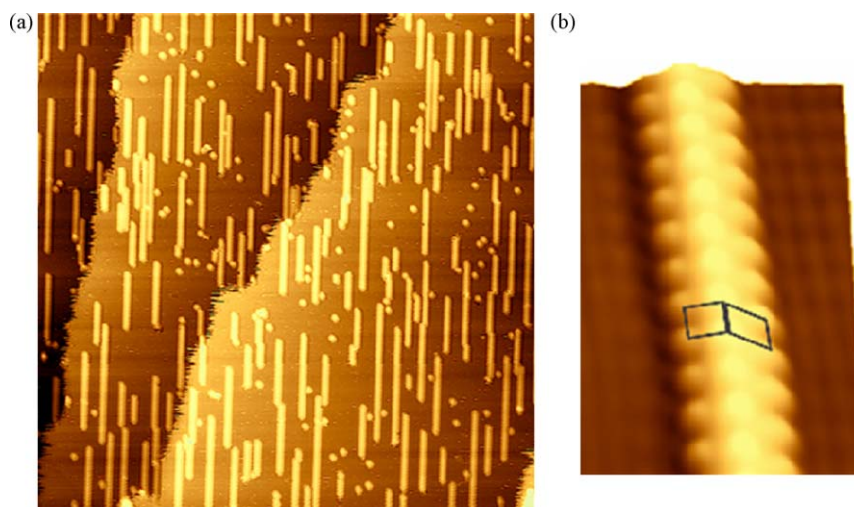

Fig. 4. (a) STM image of straight, parallel silicon nano-ribbons grown at room temperature on a Ag(1 1 0) surface (6.2 nm × 6.2 nm, *I* = 1.13 nA, *V* = −1.7 V, filled states); (b) a zoom-in at a single nano-ribbon.
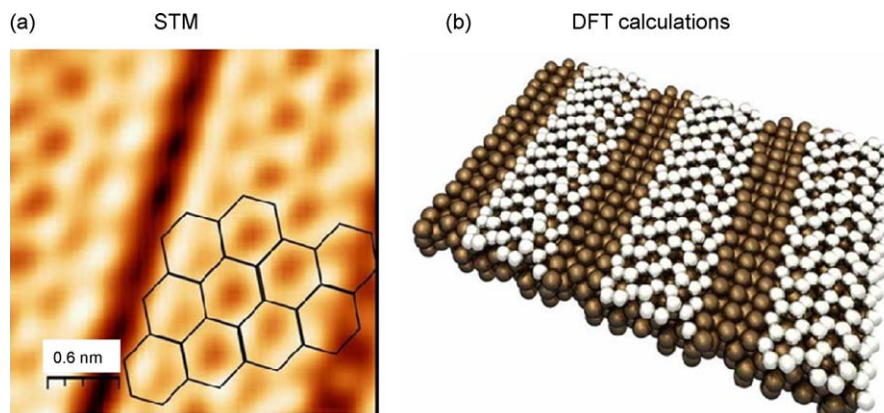

Fig. 5. Silicon nano-ribbons on Ag(110). (a) High-resolution STM image; (b) corresponding ball model of the calculated atomic structure.
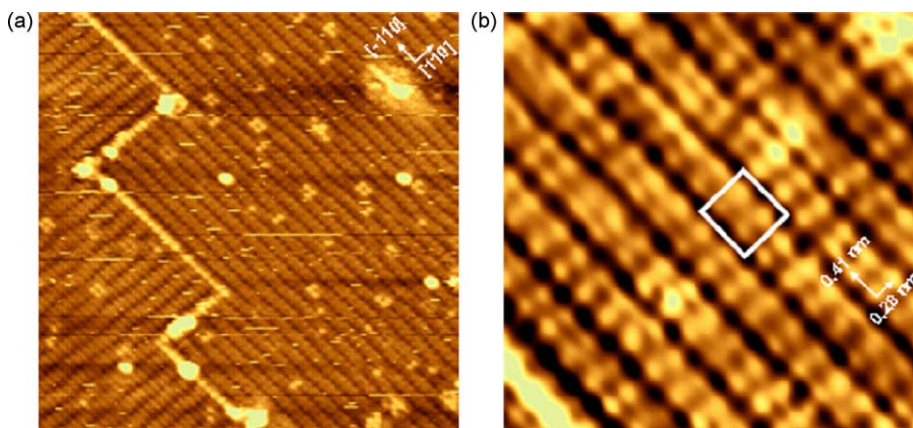
Fig. 6. (a) Filled-state STM image after the deposition of ~0.8 Si ML on Ag(0 0 1) revealing two orthogonal domains of the 3×3 superstructure (23.4 nm × 23.4 nm, $V = -1.02$ V, $I = 1.14$ nA); (b) a zoom at this superstructure (6.4 nm × 6.1 nm); the 3×3 unit cell is indicated.

Si 2p core-level lines ever met in the solid state, which testifies that they are atomically precise [20]. Unlike graphene nano-ribbons, these SiNRs do not present oxygen reactivity of the edges, making these systems more chemically stable than their graphene counterparts [21]. This behavior can be related to that of the silicon nanotubes, which are mostly non-oxidised [11]. Finally, these SiNRs can self-organize by lateral compaction to form a one-dimensional grating with a pitch of just ~2 nm [22].

The atomic geometry of these SiNRs was uncovered recently thanks to high-resolution STM images and novel Density Functional Theory calculations within the General Gradient Approximation [23].

They consist in slightly arch-shaped silicene stripes formed by a honeycomb arrangement of four hexagons, as seen in Fig. 5 [24], instead of Si dimers on top of a first adsorbed layer in hollow sites, as initially proposed [25]: such a structure is unstable when calculated in a larger cell.

2.2. On the Ag(1 0 0) surface

The first stage of the growth of silicon on Ag(0 0 1) at moderate temperatures starts by the formation of a 3×3 superstructure, which continuously evolves with increasing coverage toward a more complex superstructure, as seen in Figs. 6 and 8 [26]. We have investigated the atomic arrangement of this 3×3 structure by STM and surface X-ray diffraction (SXRD). However, the atomic model we retained for the 3×3 reconstruction, consisting in one-dimensional chains of four silicon atoms (tetramers) adsorbed near hollow and bridge sites of the top most Ag(0 0 1) surface layer, has been questioned in recent theoretical DFT calculations which point to its instability [25].
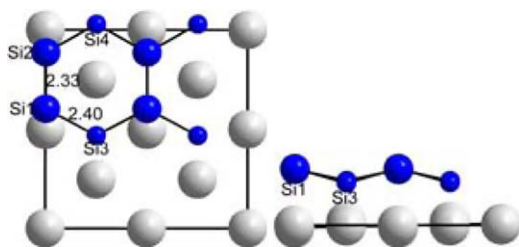

Fig. 7. Top and side views of the 3×3 structure of Si (blue balls) on Ag(1 0 0) (white balls) at 1 ML derived from DFT calculations. Atomic distances between differently labeled Si atoms are indicated [27].

Instead, a best candidate was found in terms of a hexagon-type atomic geometry at one monolayer coverage, which we can view as a silicene precursor (see Fig. 7). Indeed, this finding calls for a new analysis of our SXRD data; it will be soon undertaken.

For higher coverages, i.e., when the "complex" superstructure starts to develop, the silicon overlayer forms periodic stripes, with a silicene-like structure, as shown in Fig. 8.

For this "complex" superstructure, Guo-min He derives a silicene-type layer with extra Si adatoms residing on top, as displayed in the ball model of Fig. 8c [27]. The corresponding simulated STM image and calculated profile (shown in Fig. 8d and e) appear in reasonable agreement with the experimental image and profile (Fig. 8b and e).

3. The silicon-based analogue of graphane

Two years ago, the possible existence of graphane, a two-dimensional hydrocarbon crystal (with CH chemical formula) derived from graphene, where the carbon atoms in the hexagonal network are in the sp^3 hybridization, was theoretically conjectured [28–30]. Particularly interesting was the fact that graphane was predicted to have a direct band gap at the Γ point. Remarkably, it has just been synthesized by exposing graphene crystals to a cold hydrogen plasma (see Fig. 9) [31,32].

A key feature is that the reaction is reversible, so that the original state of graphene can be restored by annealing at a moderate temperature (450 °C in Ar atmosphere for 24 h). Strikingly, similar electronic properties, typically, a direct band gap, are predicted for the silicon analogue of graphane with SiH chemical formula [33]. This opens interesting perspectives, for example for use in optoelectronic devices, photovoltaic applications and even hydrogen storage.

The growth of silicene ribbons by molecular beam epitaxy on the silver (1 1 0) and (1 0 0) surfaces opens the route to the growth of silicene sheets on the (1 1 1) surface. Seeing the amazingly short delay between the first theoretical conjecture on graphane and its practical realization, we can anticipate that its silicon analogue may be soon synthesized.

Indeed, to this end, one can envisage to prepare silicene in large scale on thin epitaxial silver films. One could possibly remove silicene from the primary metallic substrate (eventually by soft chemistry), transfer it to an insulating support, cap it with a protective layer to make use of its unique transport properties, or instead, typically expose it to a cold hydrogen plasma to transform it eventually into a direct gap novel material similar to graphane.
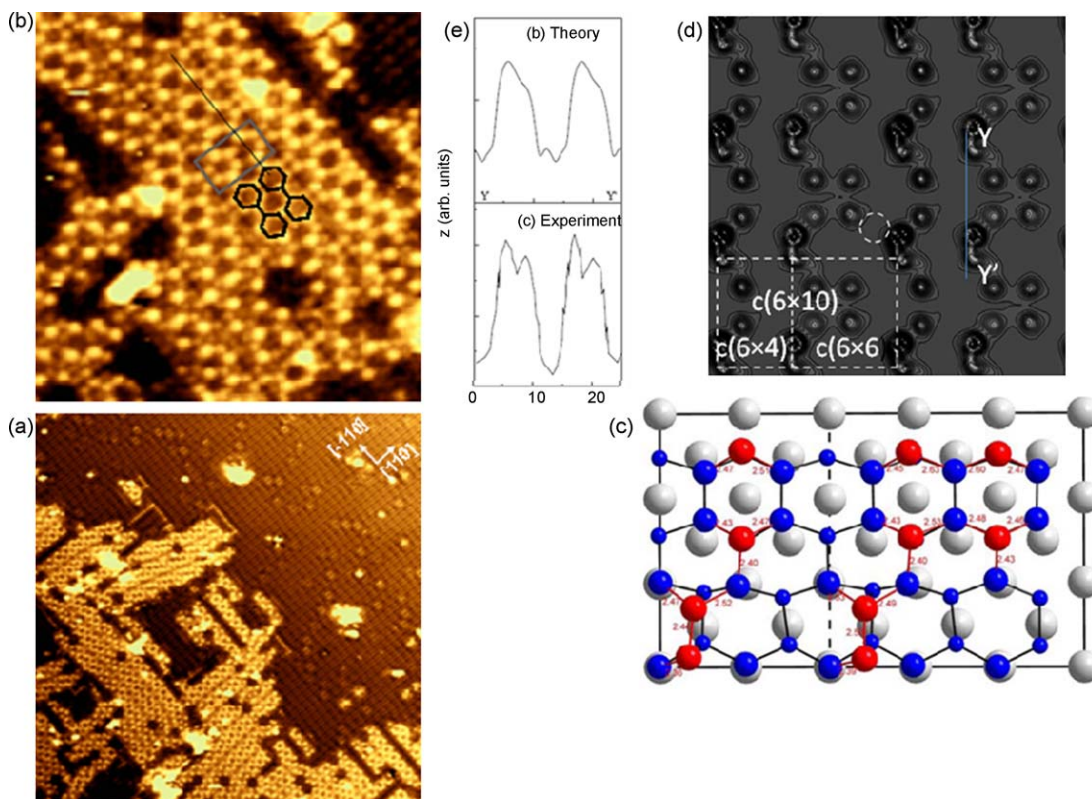
Fig. 8. (a) Filled states STM image (22.3 nm × 22.3 nm, $V = -1$ V, $I = 1$ nA) after the deposition at 230 °C of ∼1.6 Si ML on the Ag(0 0 1) surface, showing the coexistence of the 3 × 3 and the "complex" superstructures; (b) a zoom-in (6.4 nm × 6.4 nm) revealing the details of the "complex" structure: the local 7 × 4 unit cell is represented by the grey rectangle. The pattern of two joined chains of hexagons, describing the new stripes, is drawn in black. (c) Top view of the atomic model proposed by Guo-min He for this "complex" structure [27]; blue balls: Si atoms in the silicene-like layer, red balls: Si adatoms on top, white balls: Ag atoms of the Ag(1 0 0) surface; (d) simulated STM images of filled states for configuration in (c) with a bias voltage of 1.0 eV with respect to the theoretical Fermi level. The dashed lines indicate the c (6 × 10) unit cell used in the calculations; (e) shows a comparison of the calculated line profile along YY′ indicated in (d) and the measured one along the indicated direction in (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
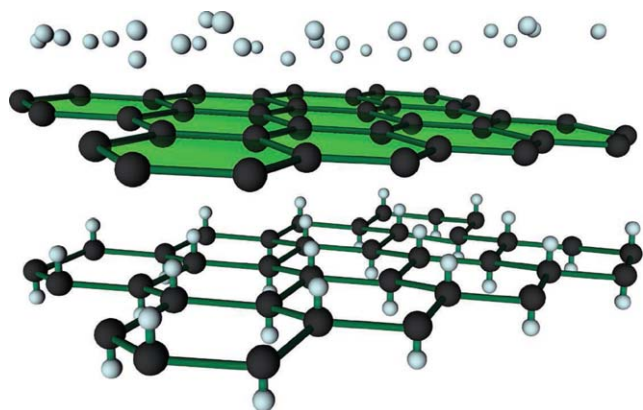

Fig. 9. Top: a graphene layer, where delocalized electrons are free to move between sp^2-bonded carbon atoms, is exposed to a beam of hydrogen atoms. Bottom: in nonconductive graphane (shown in chair conformation), the hydrogen atoms bond their electrons with electrons of carbon atoms and pull the now sp^3 hybridized atoms out of the plane. Adapted from Fig. 1 of Ref. [32].

4. Summary

The growth of silicene nano-ribbons on the (1 1 0) and (1 0 0) silver surfaces paves the way to the synthesis of silicene sheets. This crucial step in the silicene "gold rush" could give a new kick to silicon on the electronics road-map. It opens a promising route towards wide-ranging applications, eventually by further deposition of an insulating support on top and chemical removal (e.g., by soft chemistry) of the primary metallic substrate. Conversion by hydrogenation of silicene into its graphane analogue appears feasible. In the search for energy efficiency, optoelectronic devices, solar cells and hydrogen storage technologies could strongly benefit from this novel material. Another interesting path to explore is the interaction of silicene with organics, since it was recently shown that PQ molecules (9,10 phenanthrenequinone) selectively adsorb on the silicon nano-ribbons on the Ag(1 1 0) surface, thus allowing the self-organization of organic lines while opening a ∼300 meV band gap [34].

References

[1] K.S. Novoselov, et al. Science 306 (2004) 666.
[2] J. Wintterlin, M.-L. Bocquet, Surf. Sci. 603 (2009) 1841.
[3] I. Forbeaux, J.-M. Themlin, J.-M. Debever, Phys. Rev. B 58 (1998) 16396.
[4] A.K. Geim, K.S. Novoselov, Nat. Mater. 6 (2007) 183.
[5] G.G. Guzman-Verri, L.C. Lew Yan Voon, Phys. Rev. B 76 (2007) 075131.
[6] M. Takahashi, Y. Kawazoe, Comp. Mater. Sci. 36 (2006) 30.
[7] M. Moteki, S. Maeda, K. Ohno, Organometallics 28 (2009) 7.
[8] S.B. Fagan, R.J. Baierle, R. Moat, A.J.R. da Silva, A. Fazzio, Phys. Rev. B 61 (2000) 9994.

[9] X. Yang, J. Ni, Phys. Rev. B 72 (2005) 195426.
[10] D.F. Perepichka, F. Rosei, Small 2 (2006) 22.
[11] P. Castrucci, et al. Thin Solid Films 508 (2006) 226.
[12] S. Lebègue, O. Eriksson, Phys. Rev. B 79 (2009) 115409.
[13] K. Takeda, K. Shiraishi, Phys. Rev. B 50 (1994) 14916.
[14] S. Cahangirov, M. Topsakal, E. Aktürk, H. Sahin, S. Ciraci, arXiv:0811.4412v1.
[15] E.F. Sheka, arXiv:0901.3663.
[16] H. Nakano, et al. Angew. Chem. Int. Ed. 45 (2006) 6303.
[17] G. Le Lay, J. Cryst. Growth 54 (1981) 551.
[18] C. Liu, et al. Nanotechnology 19 (2008) 35520.
[19] C. Léandri, et al. Surf. Sci. 574 (2005) L9.
[20] P. De Padova, et al. Nano Lett. 8 (2008) 271.
[21] P. De Padova, et al. Nano Lett. 8 (2008) 2299.
[22] H. Sahaf, et al. Appl. Phys. Lett. 90 (2007) 263110.

[23] A. Kara, et al. J. Supercond. Novel Magnet. 22 (2009) 259.
[24] A. Kara et al., arXiv:0811.2818v1.
[25] G.-m. He, Phys. Rev. B 73 (2006) 035311.
[26] C. Léandri, et al. Surf. Sci. 601 (2007) 262.
[27] G.-m. He, Surf. Sci. 603 (2009) 2021.
[28] J.O. Sofo, A.S. Chaudhari, G.D. Barber, Phys. Rev. B 75 (2007) 153401.
[29] D.W. Boukhvalov, M.I. Katsnelson, A.I. Lichtenstein, Phys. Rev. B 77 (2008) 035427.
[30] S. Lebègue, M. Klintenberg, O. Eriksson, M.I. Katsnelson, Phys. Rev. B 79 (2009) 132102.
[31] D.C. Elias, et al. Science 323 (2009) 610.
[32] A. Savchenko, Science 323 (2009) 589.
[33] A.J. Lu, X.B. Yang, R.Q. Zhang, Solid State Commun 149 (2009) 153.
[34] E. Salomon, A. Kahn, Surf. Sci. 602 (2008) L79.
[35] S.C. Erwin, Phys. Rev. Lett. 91 (2003) 206101.