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Graphene-like silicon nanoribbons on Ag(110): A possible formation of silicene

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Scanning tunneling microscopy (STM) and *ab initio* calculations based on density functional theory (DFT) were used to study the self-aligned silicon nanoribbons on Ag(110) with honeycomb, graphene-like structure. The silicon honeycombs structure on top of the silver substrate is clearly observed by STM, while the DFT calculations confirm that the Si atoms adopt spontaneously this new silicon structure. © *2010 American Institute of Physics*. [doi:10.1063/1.3419932]

Graphene, the two-dimensional one-atom thick single layer building sheet of graphite, is probably the most investigated material in physics and nanotechnology. It has striking properties, which open potentially novel routes for many applications.[1–4] For silicon, there has been recently considerable interest in the fabrication, characterization, and properties of silicon nanostructures.[5–7] However, silicene,[8] the counterpart of graphene for silicon has not been found until now, although it has attracted strong theoretical attention since several years.[9]

In the following, we present new experimental data and theoretical calculations, which tend to reveal the epitaxial growth of silicene nanoribbons (NRs). This result stems from the search for the atomic structure of the novel one-dimensional (1D) silicon nanostructures (see Fig. 1), found recently in Marseille (France) upon growth at room temperature (RT) of silicon on silver (110) surfaces under ultrahigh vacuum conditions.[10] Let us recall that silicon was deposited at RT *in situ* from a direct-current heated piece of silicon wafer (previously flashed at ~ 1250 °C) and the surface was controlled by Auger electron spectroscopy and low energy electron diffraction.[10] These nanostructures observed with scanning tunneling microscopy (STM) were called previously silicon nanowires.[10] They are all aligned along the $[\bar{1}10]$ channels of the bare surface and display $\times 2$ periodicity along their edges. They possess the same width of just ~ 1.7 nm (i.e., about $4a_{Ag[001]}$) and show in the STM images a transverse symmetry breaking revealed in a key structure formed by a square and a parallelogram side-by-side [Fig. 1(c)]. They present a strong metallic character and a specific spectral signature: quantized states in the sp region of the valence band below the Fermi level and the narrowest Si $2p$ core-level lines ever reported in the solid state, which is the signature of an excellent atomic order.[10,11]

Unlike graphene NRs, these silicon NRs do not present oxygen reactivity of the edges, making these systems more chemically stable than their graphene counterparts.[10,11] In fact, the oxidation takes place in a peculiar mechanism starting at the extremities of the NRs with appearance of several

oxidation states similar to those observed upon the formation of the $SiO_2/Si(111)$ interface.[12] Finally, these silicon NRs can self-assemble by lateral compaction to form a 1D grating with a pitch of just ~ 2 nm covering the entire substrate surface.[13]

Soon after the publication of our first paper,[10] a possible model of these silicon NRs was proposed by Guo-min He on the basis of a density functional theory (DFT) study; it remains the sole tentative approach to elucidate their atomic structure.[14] The proposed optimum geometry presented interesting features, typically silicon dimers, the building blocks of the $Si(100)2 \times 1$ surface reconstruction. However, being constructed on a constrained 2×5 rectangular basis, the stability of this geometrical model could be eventually questioned on a larger cell (in fact the STM images in Fig. 1 show instead a $\times 4$ periodicity along the NRs; see below). Furthermore, as mentioned above, the oxidation states we have identified since then,[12] are not identical to those found upon formation of the $SiO_2/Si(100)$ interface, as would have been expected.[15]

Very recently, using the same experimental procedure as recalled above, we have obtained new STM images close to
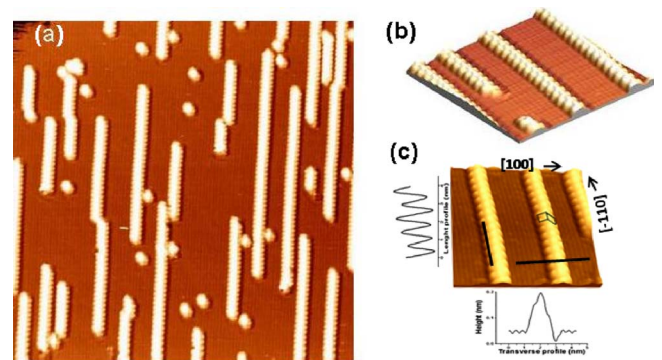

FIG. 1. (Color online) STM images of straight, parallel 1D silicon nanostructures grown on a Ag(110) surface. (a) Large view (42×42 nm^2, filled states); (b) 3D view (12×12 nm^2, filled states); and (c) detailed view (6.22×6.22 nm^2, filled states). Line profiles indicate the $2a_{Ag[\bar{1}10]}$ periodicity along each line of protrusions ($[\bar{1}10]$ direction) and the asymmetrical shape along the orthogonal direction. The geometrical aspect of the silicon NRs (a square joined to a parallelogram) is drawn in black.

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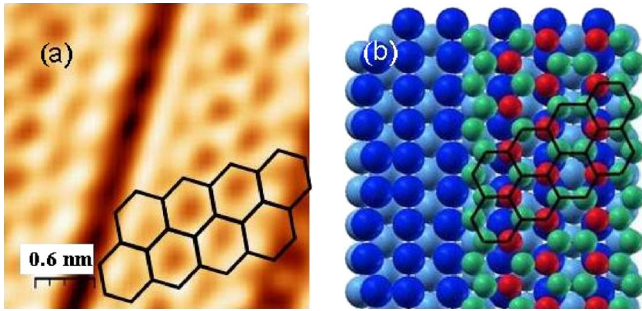
FIG. 2. (Color online) Atomic structure of silicon NRs: (a) high resolution filled state STM image revealing honeycomb arrangement (few honeycombs are drawn on the image); (b) ball model of the corresponding calculated atomic structure (large dark balls (blue)) representing Ag atoms in the first layer; top most Si atoms are represented by small dark balls (red) while others represented by light small balls (green), the whole forming hexagons (highlighted on the silicon NR).
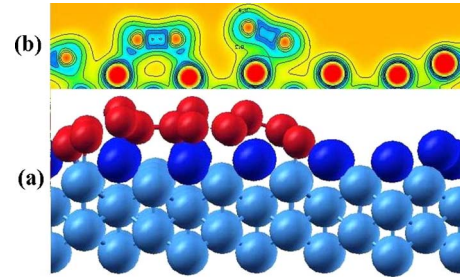

FIG. 3. (Color online) Calculated atomic and electronic structures of graphene-like silicon NRs: (a) ball model in cross section (large dark balls (blue): first layer Ag atoms and Si atoms are small dark balls (red)); (b) charge density in cross section.

atomic resolution displaying hexagons in a honeycomb arrangement, just as for graphene [Fig. 2(a)]. For such reasons it appeared mandatory to us to reanalyze theoretically the atomic structure of these silicon NRs. In the present paper, we mainly address structural aspects, leaving a detailed comparative analysis of the energetics and electronic properties of other ribbons with narrower or broader widths to a forthcoming paper.

The STM images presented in Fig. 1 show that the NRs are composed of three rows of protrusions, each with a perfect $\times 2$ periodicity, oriented along the $[\bar{1}10]$ direction of the surface. The one on the right side is shifted from the others by one $a_{\text{Ag}[\bar{1}10]}$ silver parameter, hence, the true overall periodicity is actually $\times 4$. This glide gives a transverse asymmetric structure schematically described from left to right as a square (side: ~ 0.6 nm) joined to a parallelogram, highlighted with black lines in Fig. 1(c). The crucial new experimental result is the direct evidence in high resolution STM images of four silicon hexagons in a honeycomb arrangement [see Fig. 2(a)]. The atomic geometry derived from the calculations is confronted with the usual STM images showing a square joined to a parallelogram.

Our *ab initio* calculations are based on DFT.[16,17] A comprehensive study of the energetic and the electronic structure was made by solving Kohn–Sham equations in a plane-wave basis set using the VIENNA *AB INITIO SIMULATION PACKAGE*.[18–20] Exchange-correlation interactions are included within the generalized gradient approximation (GGA) in the Perdew–Burker–Ernzerhof form.[21] The electron-ion interaction is described by the projector augmented wave method in its implementation of Kresse and Joubert.[22,23] A plane-wave energy cutoff of 250 eV was used for all calculations and is found to be sufficient for these systems. The bulk lattice constant for Ag was found to be 0.4175 nm using a k-point mesh of $10 \times 10 \times 10$. The slab supercell approach with periodic boundaries is employed to model the surface and the Brillouin zone sampling is based on the technique devised by Monkhorst and Pack[24] with a $(3 \times 2 \times 1)$ mesh. The slab consists of 5 layers of Ag(110) with only the bottom layer kept fixed, each containing 24 atoms in a (4×6) supercell, a substantial enlargement with respect to the previous theoretical work, which was performed in a 2×5 cell with three silver layers kept fixed.[14] The choice of four free layers instead of just two in Ref. 14 was made on the assumption that adsorp-

tion of the silicon NRs could eventually introduce structural perturbations to the substrate. The whole system is allowed to relax to the optimum configuration (with forces on every atom less than 0.01 eV/Å).

According to the STM image in Fig. 2(a), the silicon NRs starting configuration consists of four silicon hexagons aligned along the direction 30° from the channels of Ag(110) surface; it corresponds to 30 silicon atoms per unit cell (we name it the Si30 configuration).

In Fig. 2(b), we display the resulting Si30 optimized structure in correspondence with the high resolution STM image [Fig. 2(a)]. Note that regardless of the starting type configuration, our calculations show that the Si atoms tend to form a honeycomb structure on top of the silver substrate.

After full atomic relaxation, the atomic positions of the silicon atoms are very close to those of a slightly curved silicon NR with an average Si-Si distance of ~ 0.224 nm [Fig. 3(a)]. The cohesion energy is 95% of that of bulk silicon while the adsorption energy is only 14% pointing to a comparatively weak interaction of the NR with the substrate. Furthermore, the ribbon creates an asymmetric corrugation in the charge density profile of about 0.2 nm [Fig. 3(b)], in nice accord with the STM profiles [Fig. 1(c)].[10]

This curvature may favor the stabilization of these NRs with respect to a purely sp^2 bonded flat ribbon through intermediate $sp^2 - sp^3$ hybridizations. This "arch-shaped" configuration consists of edge Si atoms penetrating the Ag(110) channels for a better "grip" onto the surface and hence creating a "bump" in the STM images (reflecting a protrusion in the charge density). Indeed, at the edges of the NRs, there are dips that we will assimilate to "gutters" along which the energy profile is weakly corrugated. Consequently, we can assume that when Si atoms diffuse to the ribbon edges they are very rapidly dispatched to the ends of the NRs, contributing to their elongation. We believe that it is this "gutter effect" which is responsible for the formation of very long NRs at RT and above.[10]

The calculated width (from the center of the far left Si atoms to the center of the far right Si ones) is ~ 1.51 nm in good agreement with the STM images, which show an apparent width of about 1.7 nm, taking into account the van der Waals radii of the Si atoms.

The substrate itself, experiencing buckling, is somewhat altered by the NRs. The chain of silver atoms on the left of the NR is not straight and shows substantial displacements (about 0.08 nm) from the ideal positions; a new component disclosed in recent high-resolution synchrotron radiation Ag $3d$ core-level spectroscopy measurements probably
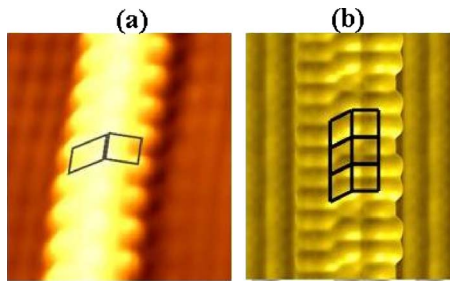
FIG. 4. (Color online) Experimental and calculated usual STM images: (a) filled state STM image of an individual NR showing the structural signature made of a square adjacent to a parallelogram (drawn in black) (3.6 × 3.7 nm^2) and (b) calculated STM image showing a similar structural signature.

stems from these displaced silver atoms. Note that it is only one side of the ribbon that is hence affected, reflecting again the asymmetric nature of the system, in good agreement with the experimental observation. The structural effects of the NRs on the silver substrate go as deep as the fourth layer because of the lateral anchoring and the softness of silver.

We further stress that the optimized Si30 configuration clearly provides also the prominent signature mentioned above, typically, the usual STM observations of a square adjacent to a parallelogram, as reproduced in the calculated STM image of Fig. 4. This demonstrates that a system of atoms like these silicon NRs, having local hexagonal symmetry, may indeed conspire in such a way to give the impression of a local square symmetry.

Let us note that Guo-min He proposed an arrangement where dimers of Si atoms formed, instead, a rectangular lattice on a (2×5) unit cell on the Ag(110) substrate.[14] We have performed calculations for this same rectangular arrangement but on a (4×6) super cell. In this case we found that not only this arrangement but also all the rectangular type geometries experience large deformations upon relaxation, with the Si atoms approaching a hexagonal configuration.

In conclusion, we have shown from the STM results at nearly atomic resolution that the self-aligned nanoribbons on the silver (110) surface present a graphene-like atomic structure, possibly pointing to silicene synthesis. This internal structure of the Si NRs is supported by DFT-GGA calculations, which show that the arrangement of 30 silicon atoms in a 4×6 unit cell on the Ag(110) surface relaxes into an arch-shaped graphene-like configuration. We recall that having the same atomic geometry as graphene, silicene possesses theoretically the same remarkable electronic features: typically, its charge carriers should be massless relativistic Dirac fermions.[8,9] In perspective, we will explore Si deposition on sixfold symmetry surfaces, such as Ag(111), in order to get continuous films of these honeycomb structures.

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