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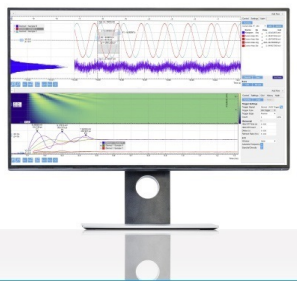

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Two-dimensional semiconducting nanostructures based on single graphene sheets with lines of adsorbed hydrogen atoms

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It is shown that lines of adsorbed hydrogen pair atoms divide the graphene sheet into strips and form hydrogen-based superlattice structures (2HG-SL). We show that the formation of 2HG-SL changes the electronic properties of graphene from semimetal to semiconductor. The electronic spectra of "zigzag" $(n,0)$ 2HG-SL is similar to that of $(n,0)$ carbon nanotubes and have a similar oscillation of band gap with n, but with nonzero minimal values. The composite dual-periodic $(n,0)+(m,0)$ 2HG-SLs of zigzag strips are analyzed, with the conclusion that they may be treated as quasi-two-dimensional heterostructures. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2800889]

The miniaturization of electronic devices has always been a driving force in electronic industry. The exciting discovery by Novoselov *et al.*[1,2] of the existence of single graphite sheets has opened possibilities in the fabrication of nanoelectronic devices based on graphene. In the last few years, a great deal of work has been dedicated to the investigation of the properties of graphene.[3]

One of the many interesting properties of Dirac electrons in graphene is the drastic changes of the conductivity of graphene-based structures with the confinement of electrons. Until now, two possibilities for the realization of this effect have been proposed: carbon nanotubes[4] (CNTs) (periodic boundary conditions for the wave vector of the electron) and graphene ribbons prepared by using electron lithography methods[5,6] (zero boundary conditions). In these structures, the band gap oscillates depending on the size, with either zero or nonzero minimal values, for carbon nanotubes[4] or graphene ribbons,[7] respectively.

In this letter, we propose another possibility of electron confinement using chemical adsorption of H atom pairs on the surface of graphene. Hydrogen lines split the graphene sheet into ribbons (electronic waveguides) with same or different electronic properties (see Fig. 1).

We show that freestanding graphene ruled by lines of covalently bonded pairs of hydrogen atoms has electronic properties similar to carbon nanotubes. The "zigzag" superlattice structures are semiconductors. Changing of width strip, i.e., period of such superlattice, leads to changing of the energy gap width of the 2H-line graphene-based superlattice (2HG-SL). Thus we can obtain set of 2D semiconductors with different properties. The present study is based upon the recent experiments with freestanding graphene sheets[8] and hydrogen dimer adsorption on graphite during annealing.[9] In another paper, it has been concluded that the barrier of hydrogen chemisorption should decrease with the elongation of hydrogen line.[10]

Our calculations were performed using density functional theory[11,12] within the local density approximation for the exchange-correlation functional.[13] Finite-range numerical pseudoatomic wave functions were used as an atomic-orbital basis set. The geometry of the structures was optimized until residual forces became less than 0.04 eV/Å. The real-space mesh cutoff was set to at least 175 Ry. The Monkhorst-Pack[14] special $\boldsymbol{k}$-point scheme was used with 0.08 $Å^{-1}$ $\boldsymbol{k}$-point spacing.

We used the SIESTA package[15,16] in all calculations. All the values given above were carefully tested and found optimal. We have investigated the dependence of electronic properties of 2HG-SLs by considering zigzag $(n,0)$ 2HG-SLs as well as dual $(n,0)+(m,0)$ 2HG-SLs [see Fig. 1(a)]. Here, 2H-lines divide a graphene sheet into zigzag $(n,0)$ strips. We have also checked the properties of freestanding (n,n) 2HG-SLs, which turn out to be semimetallic, similar to 2HG-SLs on a substrate.[17]

First, we consider $(n,0)$ 2HG-SLs. The geometric scheme of these structures is shown in Fig. 1(b). Hydrogen atoms, shown in dark (blue online), are covalently bound to C atoms, shown in light (cyan online), forming lines perpendicular to the $(n,0)$ direction in graphene. A similar scheme has been used for the investigation of hydrogenated $(n,0)$ CNTs.[18] The H atoms form local sp^3 hybridization between hydrogen and carbon atoms, which causes a local geometrical distortion of the graphene sheet, as if forming diamond-like lines.

In Figs. 1(b)–1(d), the electronic band structure of the (8,0) 2HG-SL [Fig. 1(b)] is compared with that of a (8,0) ribbon [in the conventional notation, 17-AGNR (armchair

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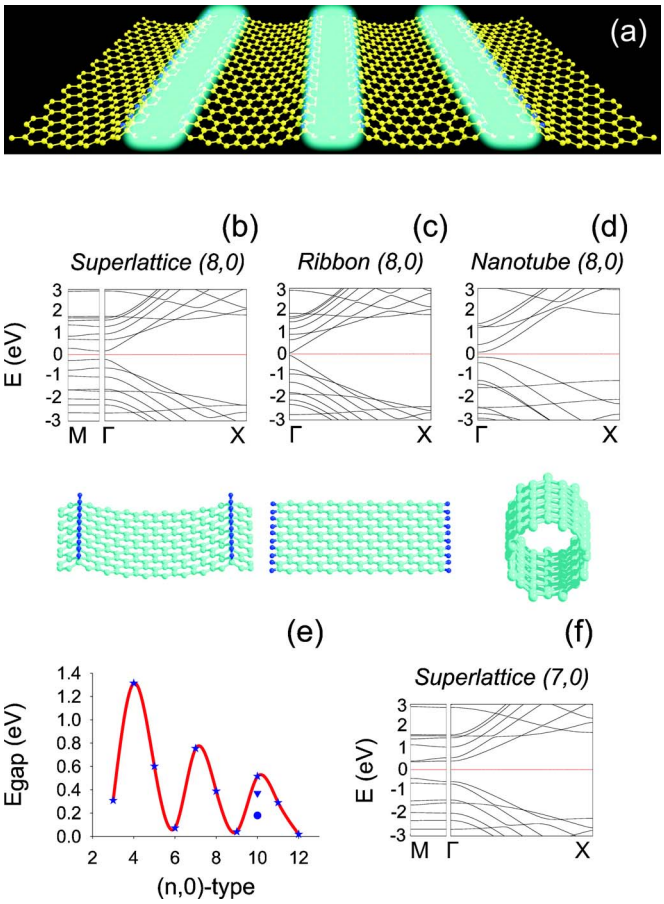

FIG. 1. (Color online) Geometry and electronic structure of 2H-line superlattice models: (a) (3,0)+(7,0) 2HG-SL scheme, where (3,0) strips (highlighted) are electronic waveguides. Band structures and corresponding views of (b) (8,0) 2HG-SL, (c) graphene ribbon (17-AGNR in conventional notation [21]), and (d) (8,0) carbon nanotubes, [carbon atoms are light (cyan online), hydrogen atoms are dark (blue online)]; (e) the variation of band gaps of $(n,0)$ 2HG-SLs as with index n [the triangle and the circle correspond to band gap width of (3,0)+(7,0) and (4,0)+(6,0) SLs, respectively]; (f) the band structure of (7,0) 2HG-SL. The Fermi level in all spectra (E=0) is marked by the horizontal line.

graphene nanoribbon)[19,7]] [Fig. 1(c)] and to the spectrum of a (8,0) CNT [Fig. 1(d)]. There is a close resemblance between all spectrums; however, in the case of superlattice, the band gap is roughly twice as large as that of CNT (E_{CNT} =0.22 eV, $E_{\mathrm{2HG\text{-}SL}}$=0.39 eV). We believe that this behavior results from confinement of electrons by the presence of sp^3-carbon-hydrogen lines (we do not compare the gap widths of the superlattice and the ribbon as the latter has a different behavior of the band gap[19,7]).

Calculations have been performed for a set of $(n,0)$ 2HG-SLs with n=3–12. We have found that band gaps oscillate with increasing superlattice width and vanish in the infinite limit of pure, semimetallic graphene [see Fig. 1(e)]. We want to mention that the oscillation of band gap of $(n,0)$ 2HG-SLs is more similar to carbon zigzag $(n,0)$ nanotube gaps oscillation[4] than to the behavior of graphene ribbon gaps.[19] In the $3n$ case, small but nonzero gaps are obtained. We suppose that the existence of nonzero gaps in the $3n$ case is connected with specific C–H bond edge effects, similarly to graphene ribbons.[7] The $(3n+1)$ 2HG-SLs with maximal band gaps have a direct gap at the M point of the spectrum, whereas other 2HG-SLs have one in Γ point [compare the

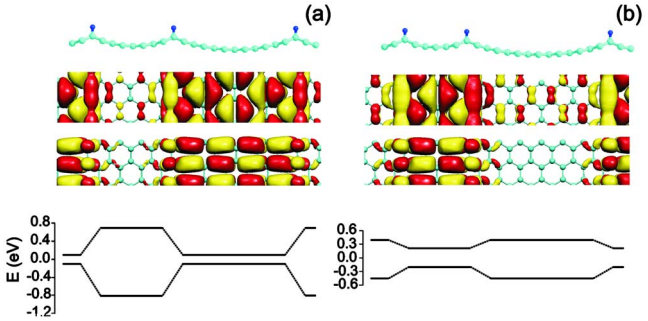

FIG. 2. (Color online) The geometrical structure, HOMO and LUMO orbitals at the Γ point (isovalue 0.02) and a schematic illustration of the energy band diagram of (a) (4,0)+(6,0) and (b) (3,0)+(7,0) 2HG-SLs.

electronic spectra of (7,0) and (8,0) superlattices in Figs. 1(f) and 1(b)].

The discussion of the origin of $3n$ dependence is important and interesting. In previous work,[17] where the 2HG-SL layer with substrate system has been investigated, van der Waals interactions cause flattening of graphene. Therefore, such a system can be roughly treated like a sequence of graphene ribbons with finite barriers between neighbors formed by sp^3 hybridized carbon atoms with strained bonds to neighboring sp^2 atoms. In the case of graphene ribbons, the oscillation of the band gap has a $3n+2$ behavior, and for the graphene-substrate system we have obtained the same result. However, in the present structures, we have a completely different situation [see Fig. 1(e)]. We believe that $3n$ dependence originate from curvature of a 2HG-SL due to the absence of substrate. The $3n$ and $3n+2$ behaviors of small-period freestanding 2HG-SLs correlate with carbon nanotubes with small diameter and graphene ribbons, respectively. The anisotropy of the 2HG-SL bands [Figs. 1(b) and 1(f)] is similar to that commonly found in superlattices of different material layers, like in $Ga_xAl_{1-x}As$,[20] but with low semiconductor gaps <1 eV (infrared region).

We have also studied composite 2HG-SLs consisting of 2H-bordered strips with different widths (see Fig. 2). The electronic spectrum $E(\boldsymbol{k})$ of such structures along graphitic strips behaves similar to the $(n,0)$-2HG-SL spectra and is not shown. The location of conduction band bottom and valence band top is determined by the strip with the larger band gap width. The geometrical scheme, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) distribution are shown in Fig. 2 for (4,0)+(6,0) and (3,0)+(7,0) structures. All orbitals are shown for the Γ point. In the case of the (4,0)+(6,0) 2HG-SL, corresponding electrons are localized near the (6,0)-strip, which, being rolled, forms the semimetallic carbon nanotube (6,0). The more "dielectric" (4,0) strip is nearly empty. In Fig. 2(a), at the bottom, the schematic band diagram of such structure is shown. We have used the technique of energy band diagram description proposed in Ref. 18, where the band offset was directly obtained from the local density of states. The dielectric (4,0) strip has low but nonzero values of local density of states in the "gap" region due to very small strip width and tunneling effect of electrons through the diamondlike barrier. The tunneling effect should be suppressed in the 2HG-SL with bigger width of the dielectric strip. The (3,0)+(7,0) structure [see Figs. 1(a) and 2(b)] has the same period of ten hexagons; however, it differs from the (4,0)+(6,0) 2HG-SL

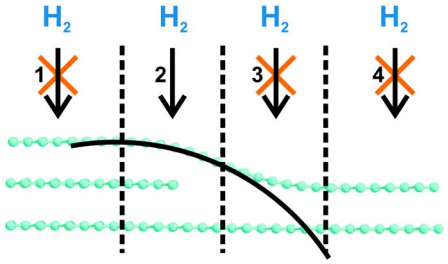

FIG. 3. (Color online) The scheme of fabrication of graphene superlattices: regions 1 and 4 are flat, while 2 and 3 have positive and negative curvature, respectively.

only in the single-hexagon shift of 2H-lines. In this case, the molecular orbital distribution is completely different. Now the (3,0) strip is filled, whereas the (7,0) strip is empty.

This effect demonstrates that an electron waveguide, a quantum nanometer wire with a "single atom thickness," can be created by decorated a "quasimetallic" $(3n,0)$ strip on graphene by two dielectric $(3n+1,0)$ or $(3n+2,0)$ strips by its sides. Thus, it can be possible to construct integrated circuits using various combinations of connected waveguides on just a single graphene sheet.

We propose a possible method of 2HG-SL fabrication. It has been shown[21,22] that the probability of hydrogen chemisorption increases with increasing local curvature of the sp^2 carbon network. Then, the bending of a graphene sheet should increase the probability of hydrogen adsorption on its surface. The formed step of graphite substrate (or of some crystalline substrate) will bend the superposed graphene sheet, as shown in Fig. 3. The curvature of graphene in region 2 is positive; therefore, this region can be treated like a fragment of a carbon nanotube. Other regions are unfavorable for adsorption: regions 1 and 4 have zero curvature and a low chemical activity, whereas in region 3 it has a negative curvature that hinders the formation of sp^3 hybridization.[21] Thus, a hydrogen line should only form in the second region during the experiment. Longitudinal shifting of graphene should flatten this region and bend another part of the sheet, thus making it possible to form periodically arranged hydrogen lines step by step.

To describe such structures, we have used molecular mechanic method,[23] which gives good qualitative description of large carbon structures.[24]

When a graphite layer step is used, the curvature radius in region 2 is equal to 18 Å. This value corresponds to the (46,0) zigzag nanotube. The longitudinal compression of the upper sheet leads to a further increase of the curvature. A strain value of 2% result in a significant decrease of region 2 curvature radius up to 8 Å, which is close to the radius of the (20,0) tube.

As-fabricated superlattices can be transferred over preliminarily prepared grooves, e.g., on the surface of SiO_2.[8] Thus, freestanding graphene-based superlattice structures with different strip widths for use as tunneling elements in nanoelectronics can be prepared.

We discuss the very important question of stability of such structures. DFT calculations show that the energy penalty (the difference of initial and final energies) for a hydrogen atom to leave the line and move away to another carbon atom is rather high, ~1.9 eV—not to mention the chemical reaction barrier. It is 1.5 times as much as the corresponding difference for H in a single adsorbed hydrogen dimer [1.17 eV (Ref. 9)]. This is a clear proof of high stability of considered 2HG-SL structures.

The present technology does not allow yet to produce the proposed structures but progress of its development gives confidence on such realization in the nearest future.

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