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Electronic superlattices and waveguides based on graphene: structures, properties and applications

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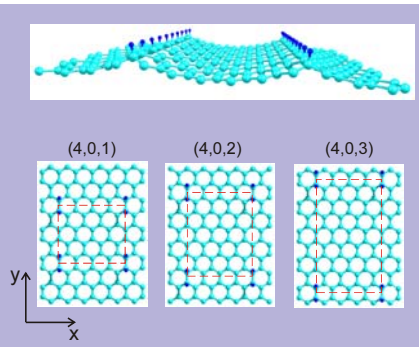
The new class of quasi-2D superlattices based on graphene with periodically adsorbed hydrogen pairs was proposed. The *ab initio* DFT method was used for optimization of the atomic geometry and electronic structure of proposed structures. It was found that the superlattices band gap decreases nonmonotonically with distance between hydrogen pairs. Based on these results we hope that the graphene superlattices can be promising candidates for various nanotechnological applications especially as elements in nanoelectronic devices.



Top: view of a 2H-line graphene-based superlattice (2HG-SL); bottom: schemes of (4,0,*k*)-2HG-SLs (*k* = 1,2,3)

1 Introduction The emergence of graphene as a stable pure two-dimensional system has been one of the most important events in electronic condensed matter physics over the last three years [1], [2]. Until recently, the 2D paradigm was limited mostly to electrons confined to quantum wells or inversion layers in semiconductor heterostructures. The situation changed three years ago when it was found that individual atomic planes could be pulled from a graphite crystal. Despite being only one atom thick the 2D crystals remained stable and proved to be nearly high perfectly crystalline and highly conductive [3].

One of the many interesting properties of graphene its Dirac type of electronic band structure and the drastic changes of the conductivity of graphene-based structures with the confinement of electrons. Such confinement can be realized in graphene by introducing new boundary conditions for wave-vector of electrons: periodic boundary conditions in the case of carbon nanotubes [4] and zero boundary conditions in the case of finite-width graphene strips (graphene ribbons) [5]. Also the periodical arrangement of defects (superlattice) on the graphene surface can lead to significant change of graphene's conductivity. For example, periodically closely spaced vacancies on a graphite sheet cause a significant rearrangement of its electronic spectrum. In the direction perpendicular to the vacancy lines, the spectrum exhibits a semimetal or semiconductor character [6]. The adatom defects' periodical arrangement also changes the electronic structure of graphene [7]. In the papers [8], [9] it was predicted that chemically adsorbed H atom pairs lines on the graphene surface split the graphene sheet into ribbons (electronic waveguides) with same or different electronic properties, forming two-dimensional superlattices.

It was shown that the free-standing graphene ruled by lines of covalently bonded pairs of hydrogen atoms has electronic properties similar to graphene ribbons. 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).

The possibility of forming of a superlattice on graphene has been confirmed by experiments (the quasi periodical hydrogen molecule adsorption during annealing on the pyrographite surface [10] and the formation of quasi periodical vacancies on the graphene sheet [11]). The 2HG-SL can be used as electronic waveguids as predicted in [9].

Another argument for the possibility of forming lines of hydrogen pairs on graphene has been made in Ref. [12] where it has been concluded that the barrier of hydrogen chemisorption should decrease with the elongation of the hydrogen line.

2 Method and model Our calculations were performed using density functional theory [13, 14] within the local density approximation for the exchange-correlation functional [15], employing norm-conserving Troullier-Martins pseudopotentials [16] in the Kleinman-Bylander factorized form [17]. Finite-range numerical pseudoatomic wave functions were used as an atomic-orbital basis set. Slabs were treated in a supercell scheme allowing enough empty space between them to make intermolecular interactions negligible. 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 [18] special ***k***-point scheme was used with 0.08 $Å^{-1}$ *k*-point spacing.

We used the SIESTA package [19, 20] in all calculations. All the values given above were carefully tested and found optimal.

3 Results and discussion

3.1 Zigzag hydrogen superlattices with fractional indexes The geometric scheme of a (*n*,0) 2H-line graphene-based superlattice is shown in Fig. 1a. Hydrogen atoms, shown in blue, are covalently bound to C atoms, shown in cyan, forming lines perpendicular to the (*n*,0) direction in graphene. 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 Ref. [9], it has been concluded that the oscillation of the band gap of (*n*,0) 2HG-SLs with integer *n* is more similar to the carbon zigzag (*n*,0) nanotube gaps oscillation.

We found that this is not a fully correct conclusion and also investigated additionally 2HG-SL (*n*/2,0) ($3 \le n \le 9$). The unit cell of structures with fractional indexes is in two times bigger than 2HG-SL with integer indexes. The result of the electronic structure calculation is presented in Fig. 1c. It is found that the band gap oscillates with increasing superlattice width (index *n*) and vanishes in the infinite limit of pure, semimetallic graphene. It is clear from the figure that 2HG-SL is a complete analog of graphene ribbons (compare Fig. 1c with Fig. 2b from [5]) and can therefore be used in nanoelectronics along with GNRs. In Fig. 1 (a and b) the comparison between 2HG-SL and GNR indexes is presented. It is possible to classify 2HG-SL as graphene ribbons as well but we used fractional indices according to our previous works [8, 9].

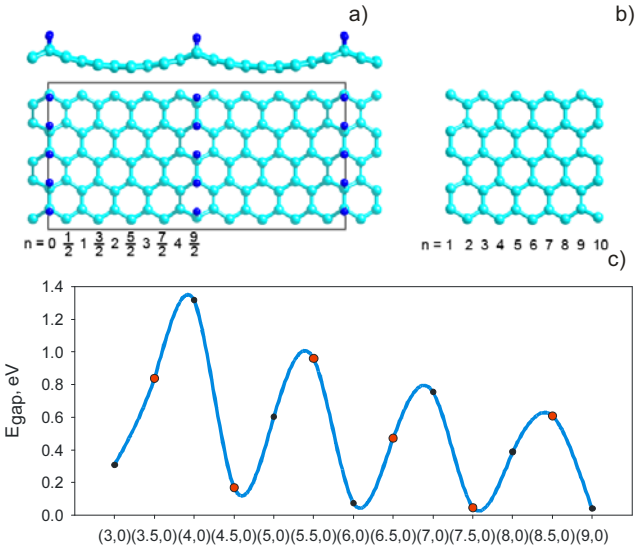


Figure 1 Geometry and electronic structure of 2H-line superlattice models. a) Side and top view of (4.5,0) 2HG-SL and comparison with b) (10,0) graphene ribbon. The unit cell of 2HG-SL is marked by a black line. c) The variation of band gaps of (*n*,0) and (*n*/2,0) (marked by gray (red online) dots) 2HG-SLs with the index *n*.

3.2 Two periodical sparse hydrogen 2H-rectangular superlattices based on graphene In experiments (e.g. annealing hydrogen molecules on graphite surface [10]), superlattices with sparse arrangement of hydrogen pairs can be obtained. A periodical arrangement of hydrogen atoms on graphene has been investigated in Ref. [21]. It has been found that the electronic properties of graphene are changed from semimetallic to semiconducting. But a systematic investigation of this effect and its origin have not been proposed yet.

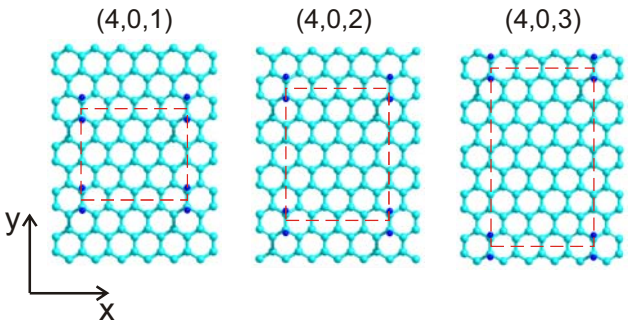


Figure 2 Schemes of hydrogen superlattices (4,0,*k*)-2HG-SLs (*k* = 1, 2, 3) (the unit cell is marked by dashed red rectangular).

For the investigation of sparse hydrogen superlattices (s2HG-SL) we added an index k to the (n,m) classification of graphene superlattices, where k is the number of graphene hexagons separating hydrogen pairs (see Fig. 2). We considered only rectangular $(n,0,k)$ 2HG-SLs which have two periods: one equals $\approx \sqrt{3}nd_{C-C}$ (n hexagons along the x-axis, $d_{C\text{-}C}$ is the distance between nearest carbon atoms ≈ 1.42 Å), the other equals $\approx 3(k+1)d_{C-C}$.

The band gap's behavior with increasing SL period along the x-axis is shown in Fig. 3. Calculations have performed for a set of $(n, 0, k)$ 2HG-SLs with $n = 3 - 12$ for different k ($k = 1, 2, 3$). We found that band gaps oscillate with increasing superlattice width and vanish in the limit of infinite of graphene. Also the band gaps width decreases with increasing space between hydrogen pairs (SL period along the y-axis). An interesting fact is that the band gap decreases nonmonotonically for $(3n - 1, 0, k)$ 2HG-SL (see Fig. 3b). The $(3n - 1, 0, k)$ 2HG-SLs have semiconducting properties when $k < 3$ whereas superlattices with other indices became semimetals for any non-zero k value. The $(3n - 1, 0, 1)$ 2HG-SL have a bigger band gap than the $(3n - 1, 0, 0)$ 2HG-SL.

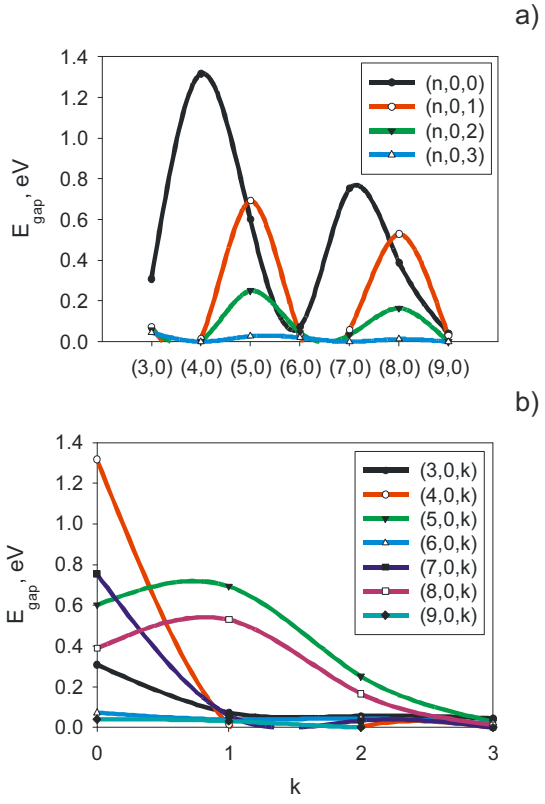


Figure 3 a) The variation of band gaps of $(n,0,k)$-2HG-SLs for different n number (the black line with filled circles corresponds to the $(n,0,0)$ case, the black (red online) line with empty circles to $(n,0,1)$, the gray (green online) line with filled triangles to $(n,0,2)$ and the gray (blue online) line with empty triangles to $(n,0,3)$); b) $E_{gap}(k)$ behavior for $(n,0,k)$-2HG-SLs with different n (the black line with filled circles corresponds to (3,0,k), the black (red online) line with empty circles to $(4,0,k)$, the gray (green online) line with filled triangles to $(5,0,k)$, the gray (yellow online) line with empty triangles to $(6,0,k)$, the black (blue online) line with filled squares to $(7,0,k)$, the gray (pink online) line with empty squares to $(8,0,k)$, the gray (cyan online) line with filled diamonds to $(9,0,k)$.

The effect of the nonmonotonically decreasing band gap of 2HG-SL with increasing k can be useful in nanoelectronics applications.

The superlattices described above can be prepared by annealing hydrogen molecules on a graphite surface [10]; after that superlattices can be transferred over preliminarily prepared grooves, e.g., on the surface of SiO_2 [22]. The technique in Ref. [9] can also be used.

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