Electronic and magnetic properties of zigzag graphene nanoribbon-based 1D superlattices

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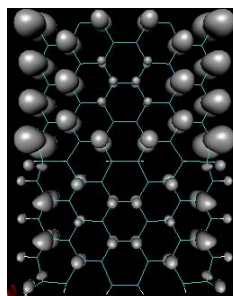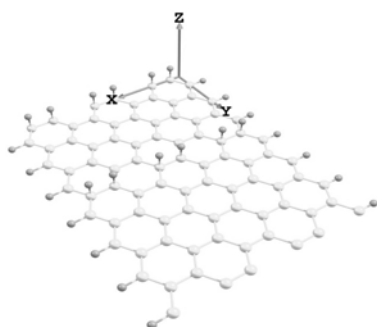
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Recently, a lot of attention is being paid to graphene-based nanostructures, owing to their unique physicochemical properties. In particular, substantial interest is devoted to graphene nanoribbons, which exhibit a number of interesting edge-related phenomena. These effects and the quasi-1D nature of nanoribbons make them an interesting candidate for future nanoscale electronic and spintronic devices.

The present work deals with zigzag-edged graphene nanoribbons, which have previously been predicted to have interesting magnetic properties near the edges [1]. Using density functional calculations, we demonstrate that such nanoribbons can be subdivided into series of isolated 'quantum dots' by transverse lines of chemisorbed hydrogen atoms. The resulting sp3-hybridized regions effectively isolates the regions between them from each other, creating a 1D superlattice of graphene quantum dots. The electronic structure of such a superlattice represents a set of flat minibands; the valence—conduction band gap is considerably increased with respect to pure nanoribbons. Furthermore, the magnetic interactions between edge states within each quantum dot and between the dots give rise to a rich and complex spectrum of magnetic states.

In this work, we explore the different possible magnetic ordering states in such structures and the complex interplay between them. The prospects of using such structures in future nanospintronic devices is considered.

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Dynamics of spontaneous deformations of graphene nanoribbons

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Recently the electronic and magnetic properties of graphene structures attract a lot of attention. However also the big interest is caused with their geometrical and mechanical properties that are most interestingly shown in graphene of the finite sizes. nanoribbons is the most interesting structures in this area.

In pristine graphene ribbons, disruption of the aromatic bond network results in depopulation of covalent orbitals and tends to elongate the edge, with an effective force of fe ~ 2 eV/E (larger for armchair edges than for zigzag edges, according to calculations). Graphene ribbons are very flexible, "flimsy" objects so this edge force can have quite striking macroscopic manifestation in case of narrow ribbons as difficult random shape of structures at 700K (for structures with both types of edge) and as it favours their spontaneous twisting for armchair-structures and forming wavelike structures with periodic perpendicular curve for zigzag-structures at 0K. Through atomistic simulations, we investigate how the torsion ф~лt decreases with the width of the ribbon, and observe its bifurcation: the twist of wider ribbons abruptly vanishes and instead the corrugation localizes near the edges. The length-scale (ле) of the emerging sinusoidal "frill" at the edge is fully determined by the intrinsic parameters of graphene, namely it's bending stiffness D=1.5 eV and the edge force fe with ле~D/fe. Analysis reveals other warping configurations and suggests their sensitivity to the chemical passivation of the edges, leading to possible applications in sensors.

Graphene biribbons: the features of electronic properties.

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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 years. Shortly after the isolation of graphene it was found that the electronic structure of few layered graphene strongly depends from the number of layers. The stimulating properties of single and double graphene layers give promising that the ribbons (finite-width graphene strips) should have similar properties. We studied the biribbons electronic properties in this work.

The calculations of electronic structure of ribbons and biribbons were performed using density functional theory within the local density approximation for the exchange-correlation functional. This numerical technique, in spite of not explicitly accounting for the van der Waals part of the interlayer interaction, has been proved to give the correct equilibrium structure and to be accurate enough to tackle the complex band structure of 3D graphites in the vicinity of EF and few-layer graphene

We found that the band gap of the biribbons strongly depends from the ribbon type (we studied both armchair-type and zigzag-type ribbons) and width. We studied the electronic structure of composite armchair-zigzag ribbons.

We investigated the possible cross-type orientation of ribbons. In this case we found the quantum dot in the region of ribbons contact

New cabon materials: modeling nanotube- graphene nanoribbons composites

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Recently the electronic and magnetic properties of graphene structures attract a lot of attention. The special graphene feature plays an important role in the electronic structure of carbon single walled nanotubes (SWNT) and graphene nanoribbons (GNR) whose conductivity type depends on the coincidence of the allowed wave vector with the Dirac points of graphene. SWNT and GNR possess unique mechanic properties. That is why we began to study new symbiosis structures formed by SWNT's and GNR's [1].

We consider the reaction covalent addition zigzag (Z) edge or armchair (A) edge of GNR's to a SWNT of different chirality. Between them more stable structures are Z-edged GNR covalent bonded with (n,n) SWNT's and A-edged GNR covalent bonded with (n,0) SWNT's. The covalent bonding change drastically symmetry both nanotubes and nanoribbons. Each considered cbGNR -SWNT structure has "finger print" Van Hove peculiarities of electron spectrum similar separate SWNT's (or GNR's), and so they can be identified by Raman studies. We have studied free standing molecular bonded (mb) GNR -SWNT structures by molecular dynamic (MD) methods and showed that all nanoribbons align along nanotubes and take the form similar a part of cylinder. MD studies of considered quasi one-dimensional and two- dimensional cb-GNR-SWNT and mb-GNR -SWNT structures have showed high anisotropic elastic effects.

The calculations of reaction process were carried out in a single-determinant unrestricted Hartree-Fock approximation [2]. The calculations of electronic properties were made by DFT method using SIESTA program.

We have modeled also multi-terminal (T- and X- types) mb-GNR -SWNT junctions and their electronic properties.

Some applications these structures (as components of elastic and conducting composites, optics and electronic elements, and so on) are considered. The work was supported partly by RFBR project N. 08-02-01096 and RAN program N 27.

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Chemical reactivity and magnetism of graphene

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The basic problem of weak interaction between odd electrons in graphene is considered within the framework of broken spin-symmetry single-determinant approach. The modern implementations of the approach in the form of either unrestricted Hartree-Fock scheme (UBS HF) or spin-polarized DFT (UBS DFT) were discussed with particular attention to the applicability of spin-contaminated solutions of both techniques for the description of electronic properties of graphene. The UBS DFT applications generally reveal the open-shell character of the singlet state of the object and manifest an extra spin density concentrated on zigzag edge atoms (see [1] and references therein). Similarly, the current study shows that UBS HF approach supports these findings but exhibits the extra spin density not only on zigzag edge atoms but on all atoms of the sheet. This very peculiarity permits to quantitatively describe the odd electron behavior via both enhanced chemical reactivity and magnetism. The former is presented in terms of a quantified atomic chemical susceptibility that is homogeneously distributed over all nonedge inner atoms with the value similar to that of fullerenes and CNTs sidewalls and is twice or five times more on zigzag edge atoms depending on if those are either terminated (by hydrogen) or empty. Armchair edge atoms 4 times prevail over inner ones only in the absence of chemical termination. Magnetic response of graphene sheets is provided by a collective action of all odd electrons and is size-dependent. The relative magnetic coupling constant J decreases when the sheet size increases and J approaches the limit value of 10^{-2}-10^{-3} kcal/mol, needed for the object magnetization to be recoded, when the sheet size is of a few *nm* that is well consistent with experimental findings [2].

The explanation suggested by the UBS HF approach seems quite reasonable. A common view on both chemical reactivity and magnetism of graphene, physically clear and transparent, witnesses the approach internal self-consistency and exhibits its high ability to quantitatively describe practically important consequences of weak interaction between odd electrons. The statement is well supported by a deep coherency of the obtained UBS HF results with those followed from the application of many-body CI calculation schemes to acenes [3] and graphene [4].

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Simple estimations of the elastic characteristics of graphene and silicene

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Graphene and silicene are the monolayer of carbon or silicon atoms packed into two-dimensional (2D) honeycomb lattice. In paper [1] the modified Harrison's bond-orbital model (BOM) has been used for the estimations of the grapheme binding energy. Here we will use the same scenario for the graphene and silicone force constants.

We begin with the bonding energy expression (per atom) for the 2D atomic layer of the carbon or silicon atoms [1]: $E_{atom}^{2D} = -3|V_2|[1 - S + (3/4)(V_1/V_2)^2]$, where V_2 is the covalent energy of the σ-interaction of sp^2-orbitals, V_1 is the metallic energy, and S is the overlap integral. Introducing the bond-stretching force constant $k_0 = (\partial^2 E_{atom}^{2D} / \partial d^2)_{\bar{d}}$, where $\bar{d}$ is the equilibrium nearest-neighbor separation for the carbon or silicon layer, we find $k_0 = (3|V_2|/\bar{d}^2)[-4 + 9S - (3/2)(V_1/V_2)^2]$. The bond-banding force constant can be defined as $k_1 = \bar{d}^{-2}(\partial^2 E_{atom}^{2D} / \partial \vartheta^2)_{\vartheta=0}$, where ϑ is the angle of the sp^2-orbital rotation from the equilibrium direction of the σ-bond. It can be shown that $k_1 = (6\lambda|V_2|/\bar{d}^2)[1 - S - (V_1/V_2)^2]$, where λ is the parameter, which depends only on the type of hybridization ($\lambda = 0.66$ for sp^2 and 0.85 for sp^3).

The calculated results are shown in Table, which includes also the results for the bulk diamond and silicon. To obtain these latter results one has to multiply all formulas by $4/3$ and use the sp^3-orbitals for the calculations of V_2, V_1. It is clear from Table that k_0 for the 2D structures are greater than for the 3D ones, while for k_1 one has the opposite inequality.

force constant	graphene	diamond	silicene	silicon
k_0, N/m	530	500	60	50
k_1, N/m	124	147	16	22

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Formation of a highly porous graphene-based material with Pt nanoparticles by intercalation of $[Pt(NH_3)_4]^{2+}$ into graphite oxide

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GO just as graphite has a layered structure, but its polyaromatic character is lost due to the appearance of oxygen-containing functional groups. Nevertheless it also has a unique capability to form intercalation compounds and therefore offers great opportunities for the production of the carbon material wherein the whole "intrinsic" graphite surface is utilized for the deposition of metal particles. Molecules of intercalated species fill interlayer spaces and form monomolecular layers during intercalation process. Due to the electrostatic attraction molecules anchor to the surface groups and don't agglomerate strongly during material processing.

A high-porous composite material (BET surface 650m^2/g) consists of crumpled graphene sheets with platinum nanoparticles has been synthesized via thermal decomposition of the graphite oxide (GO) with intercalated $[Pt(NH_3)_4]^{2+}$ ions. Due to the charge interaction positive $[Pt(NH_3)_4]^{2+}$ ions are attracted to the negatively charged surface of GO and cover it uniformly. Thermal treatment of the obtained composite leads to the partial elimination of surface groups from the GO and decomposition of platinum complexes. Owing to the high thermal stability of surface groups even after 600°C treatment graphene layers still contains some amount of oxygen mainly in the form of carbonyl groups which play a crucial role. On the one hand, they serve as anchoring centers for the platinum particles and, on the other hand, are responsible for observed graphene sheets curvature. Thus, exfoliation caused by evolved gases gives rise to the partially oxidized carbon material with turbostratic graphite morphology decorated randomly by platinum nanoparticles with a size ranges from 2 to 5nm.

Influence of substrate's material on the structure graphene films synthesized by thermal-electric method

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It is known that the graphite monolayer (graphene) is characterized by high mobility of electrons. This makes graphene a very perspective material for various nanoelectronic devices possessing the highest speed of response and low power consumption.

We studied influence of substrate's material on the growth of graphite films which were synthesized by method thermal-electric sputtering the carbon electrodes in vacuum and were annealed at different temperatures. It is known that the substrate material makes considerable impact on process of formation carbon nanotubes. Therefore it was represented interesting to learn a role of substrate material in the process of growth of the graphene layer.

We used as substrate following materials: Si (110), SiO_2/Si, corundum and quartz. The growth of films on the different substrates was occurred at single technologic process. Evaporation of graphite electrodes was spent in a pulse mode. At pulse duration 2 sec and number of impulses 50 the thickness of films was ~ 0.16 mkm. The temperature of substrate was 300-400K. For relieving elastic stress the films were annealed at temperature 1020°C during 5 min with following cooling-down in vacuum 3…4 hours. Structure of received films was studied by methods of tunneling and scanning electron microscopy, atomic-force microscopy and transmission electron microscopy. In addition we supervised the resistance of films before and after their annealing. Received results allow to draw a conclusion about influence of substrate material on the process forming the carbon film structure.

The possible mechanism of growth of carbon films will be discussed.

The theoretical study of mechanical properties of graphene membranes

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The mechanical properties of the single graphene membranes were investigated by classical molecular dynamics (MD) simulation method.

Graphene is the graphite layer with atomic thickness, and corresponds actually a two-dimensional object [1]. The excellent thermal conduction property of graphene is beneficial for the possible electronic applications [2]. Its intrinsic strength, predicted to exceed that of any other material [3].

The main goal of this work is the theoretical investigation of mechanical properties of graphene membranes using MD simulation method. The graphene membranes of different diameters from 38 Å to 140 Å were studied and they Young's module was calculation.

The theoretical study is based on experimental work [3]. The cone of the frozen atoms (modelling the atomic force microscope cantilever) strains the graphene membrane. The dependence of Young's modulus from the diameter of membrane was obtained.

It was found that the Young's modulus of membranes for diameters larger than 100 Å corresponds to experimental value 1.1 TPa [3].

Also we investigated graphene membranes with vacancy defects of different concentration from 0.25% to 7%. It is interesting that Young's modulus of graphene with defects concentration less than 1% increased nearly in two times (from 1.35 TPa (0%) to 2.57 TPa (1%)) and decreased with further increasing defects concentration. The origin of this effect was discussed.

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Interlayer tunnelling spectroscopy of Dirac fermions in graphite

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Using double sided etching of thin single crystals of graphite with focused ion beam we fabricate stacked nanostructures for studies of interlayer tunnelling in graphite. The structures have micron lateral sizes and contain few tens of graphene layers [1].

The interlayer tunneling spectra of graphite mesas under magnetic field oriented across the layers (B = 0.4-6 T) show the peaks, which can be identified as transitions between Landau levels (LLs) with numbers N = 1, 2, 3 in valence band and N′= N in conduction band. The energy of the peaks and their square root dependence on NB corresponds to relativistic LLs observed in graphene by magneto-transmission experiment [4]. Our results are consistent with recent observations of Dirac fermion features in graphite by ARPES [5], STM [6] and magneto-transmission [7] methods.

The interlayer tunneling spectra have also been studied in pulsed magnetic field up to 55 T. In parallel magnetic field above 25 T we found the local maximum on interlayer tunnelling conductivity which position V is proportional to the field. We consider that the tunneling between graphene layers in parallel field change Dirac fermion momentum by $\Delta k = 2\pi eBd/(hc)$ with d the interlayer spacing. The increase of tunnelling current occurs when shifted spectra touch tangentially at $V = hv_F \Delta k/(2\pi e)$. The estimation gives V=50 mV at 55T which is close to the experiment.

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Optical transmission spectroscopy for characterization of absorption due to surface plasmon resonance in multi-shell nanographites

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Optical transmission spectroscopy is a powerful tool for testing the optical extinction properties of nanocarbons with an extended π-electron system (nanotubes and nanographites) which have been a subject of special interest for the last decade.

Nanographite (NG) particles were produced by annealing of detonation nanodiamonds (grain size ~5 nm) in argon flow at 1600°C during various exposure times which were taken between 2 min and ~2 h, as described in [1]. The obtained NG powders were used for further preparation of water suspensions of NG particles. A series of various NG suspensions were prepared by repeated controlled dilution of initial dense suspension.

The aim of the present study is to find the correlation between the electronic (ESR) properties of NG and optical absorption of NG suspensions during the nanographite transformation (re-shaping) as a function of annealing duration time at 1600ºC. According to the HRTEM observations, the annealing transforms the nanodiamonds into quasi-spherical carbon onions nearly completely after the first 2 min of the process. Further graphitization converted them to polyhedral NG particles with an empty core. For the samples studied the mean inter-layer spacing between the graphitic shells is 0.345 nm, which is greater than the 0.335 nm spacing for bulk graphite. It means the ''turbostratic'' character of NG particles.

Optical transmission spectra were recorded in the spectral range of 200-1100 nm. Certain characteristic features around 255 nm related with surface plasmon resonance (SPR) were found on all optical extinction spectra of NG suspensions. Surface plasmon excitation is responsible for appearance of broad absorption peak around 255 nm. The observable redshift of SPR respecting the SPR in vacuum medium (~217 nm) can be explained by the water environment and aggregation effect of NG particles. The observed changes in the optical extinction spectra of the NG suspensions are attributed to the development of an extended π-electron network during the graphitization.

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Graphene layers on Rh(111)

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Earlier, we have studied in detail nucleation and growth of graphene layers on various metals Ir(III), Ir(I00), Re(I0I0), Pt(III), Ni(III), and Mo(I00). The present paper concerns graphene formation on Rh(III). The experiments were carried out in ultrahigh vacuum high resolution ($\Delta E/E \leq 0.1\%$) Auger spectrometer. The samples were thin grain-oriented ribbons measured ($1 \times 0.02 \times 40$) mm, uniform in work function ($\varphi = 4.95$ eV) with (111) face on the surface. The surface probing by CsCl molecular flux has been used, the method being very sensitive to graphene phase and allowing one to measure its relative area quantitatively with a high precision.

Rhodium heated to T = 1300K was exposed to benzene vapor ($P_{C6H6} \sim 10^{-5}$ Torr), C_6H_6 molecules to be broken up, hydrogen to desorbs, and carbon to dissolve in metal bulk. After achievement of the solubility limit for the used temperature, about 0.1 atomic %, graphene islands nucleate on the surface, grow, merge, and produce a continuous layer as a result.

Earlier we have shown that graphene on metal surface shows emission, catalytic, adsorption, and other physical properties inherent for basal graphite face, and can be treated as a two-dimensional crystal.

Adsorption passivity of graphene results in a cease of C_6H_6 dissociation, and the film thickness remains constant. Molecular CsCl also ceases to dissociate, only some residual dissociation takes place at the level of 0.1% probably due to structural defects – the edges of merged islands.

Graphene surface is uniform in work function with $\varphi = 4,35$ eV. A weak bond to Rh surface gives rise to an interesting effect – intercalation of foreign atoms, like K or Cs: they come behind the layer spontaneously and store between the graphene and the surface in considerable amounts about 1 monolayer. If one lowers the temperature, e.g. to T = 1100 K, the solid solution Rh-C become oversaturated, surplus carbon atom precipitate onto the surface to build a poly-layer graphite film. Contrary, a temperature increase up to T = 1500K results in fast destruction of a graphene layer, and only chemisorbed carbon presents on the surface with concentration $\sim 5 \cdot 10^{14}$ atoms / sm^2. Thin metal samples and active carbon diffusion in Rh, leads to fast reversal processes observed in the carbon adsorption layer with a temperature change.