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Molecularly and atomically thin semiconductor and carbon nanoshells

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Approaches to the formation of molecularly and atomically thin solid shells based on the transformation of thin planar films into more functional 3D precise shells are outlined. In the overview part of the present work several examples are given illustrating the possibility to obtain in bent films new effects never observed in planar films and to fabricate new nanomaterials from highly – ordered systems of interacting hybrid shells. In the original part of the article, we demonstrate the formation of nanoshells from monoatomic graphite layers, graphene, and also show the possibility of controllable detachment of graphene from graphite substrates with the help of AFM.

1 Introduction

An urgent problem in developing high-performance nanodevices and nanosystems is overcoming the limitations of planar integrated-circuit and nanomachining technologies. An approach to solving this problem for semiconductors, dielectrics, metals, semimetals and hybrid structures was described in [1, 2] and reviewed in [3–7]. The proposed approach is based on controllable detachment from substrates of ultra-thin epitaxial heterofilms with thickness down to monolayers followed by their transformation, under the action of internal lattice mismatch induced strains, in variously shaped nanoshells, including tubes, corrugations, scrolls, fibers, rings, helices, etc. [1–7]. The method combines the advantages of the well-established planar technology and the high atomic precision of epitaxial growth processes for strained monolayers. Precise 3D structures fabricated in this way offer much promise as building blocks for nanoelectronic and nanomechanical devices, and for creating novel materials [3–7].

In the overview part of the present work several examples are given illustrating the possibility to obtain in bent films new distinct effects never observed in planar films and to employ highly-ordered systems of interacting hybrid shells in fabricating new materials presenting analogues to organic optically active materials and metamaterials with properties never found in nature.

In the original part of the present short article, we demonstrate, for the first time, the formation of nanoshells from monoatomic graphite layers, graphene, and also demonstrate the possibility of controllable detachment of graphene from graphite substrates with the help of AFM.

2 Study and application of semiconductor and hybrid shells

Here, we will consider briefly just one result in studying the transport of two-dimensional electron gas on a cylindrical surface [8–16]. A Hall bar provided with contact pads was prepared on a starting planar

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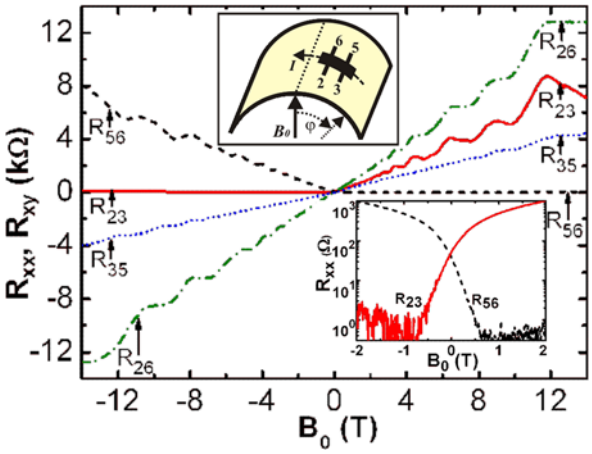

Fig. 1 (online colour at: www.pss-b.com) Longitudinal and transverse resistances of the cylindrical two-dimensional electron gas vs. magnetic field measured for different orientations of one and the same Hall bar with respect to the magnetic-field direction. The upper inset shows the experimental geometries, and the lower inset shows longitudinal resistances vs. magnetic field on a logarithmic scale. The direction of the current I and the direction of the external magnetic field B_0 are shown with the dashed line and solid arrow, respectively. The resistances measured between different pairs of probes 2, 3, 5, and 6 are indicated with subscripts.

structure with the help of standard planar lithography. Then, the film with the formed specimen was detached from the substrate and rolled up in a shell [8]. The insert in Fig. 1 shows a schematic of the fabricated bent film with the Hall bar. In such bent structures, ballistic electron transport on curved surface [16] and giant magnetoresistance asymmetry (10^3) were observed [15]. Figure 1 shows the resistances R_{xx} and R_{xy} as functions of the magnetic field B_0 for different combinations of contacts in the curved InGaAs/GaAs Hall bar. The asymmetry consisted in the fact that, for the given current direction indicated in Fig. 1 with the character I, the measured resistance R_{23} strongly increased with the magnetic field (see the range of positive magnetic fields in Fig. 1). With the magnetic-field direction changed to the opposite the resistance vanished abruptly (see the insert to Fig. 1) to become independent of the magnetic-field intensity. This unusual behavior displayed by magnetoresistance was due to the fact that the transport of charge carriers was influenced by the surface-normal magnetic-field component only.

As it is seen from the insert to Fig. 1, in the case of a bent sample placed in a uniform magnetic field this magnetic-field component strongly varies over the curved surface. In real magnetic fields the magnetic-field gradient can run into values amounting to 10^4 T/cm and 10^7 T/cm for shells with micrometer and nanometer curvature radii. It is the presence of the magnetic-field gradient and the change of its sign on reversing the field polarity that are responsible for the observed magnetoresistance asymmetry. This asymmetry was quantitatively analyzed in terms of the Landauer–Büttiker formalism [15, 17].

Development of micro- and nanostructuring brought into life novel artificial electromagnetic media – materials with negative refractive index, high-frequency magnetics, chiral materials, nonreflective materials, non-reciprocating artificial media etc. [18, 19]. They are often called metamaterials so as to emphasize that their properties are gained not from atomic or molecular level structure, but from the artificial structure- resonator of larger scale, that is still not large in comparison with the wavelength of radiation and allows describing its electromagnetic properties with some integral characteristics used for common materials, such as absorption coefficient or dielectric permittivity. Metamaterials are expected to find applications in telecommunication, information storage and processing, lithography, microscopy, biomedicine and other areas in which unprecendented control of electromagnetic radiation is required.

The artificial plane elements – resonators have the following disadvantages in the fabrication of metamaterials: they allow no coupling with in-plane magnetic-field component, no electric coupling with normal electric-field component, and no control of μ_x, μ_y, and dielectric permittivity ε_z.

3D nanoresonators can be fabricated from 3D nanoshells. A promising field where 3D shells can find application is the development of metamaterials with negative refraction and optically active materials. The approach developed in our works can be used to create chiral spiral structures [20, 21], optically active materials [20], and metamaterials based on optically active materials. Arrays of precise hybrid metal-semiconductor microhelices were recently fabricated from strained bifilms [20]. Rotation of the

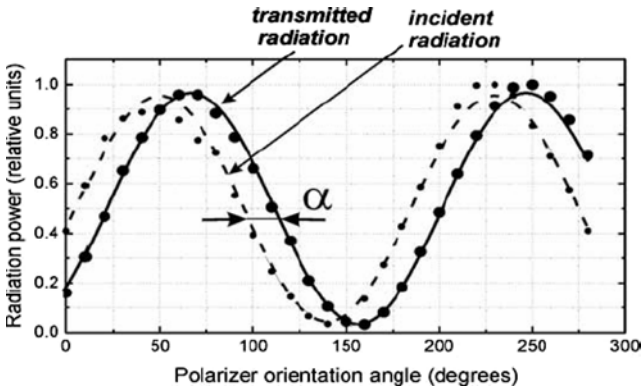

Fig. 2 Radiation power as a function of polarizer orientation angle (λ = 142 μm, α = 17°).

polarization plane of radiation by arrays of helices in microwave and THz ranges was examined in [20] (Fig. 2). The maximum angle of polazation plane rotation in microwave range (135–145 GHz), close to 90°, was achieved for an array of parallel helices, oriented parallel to the wave line, with pitch close to the wavelength of the microwave radiation.

Scalability of the effect and the used nanostructuring technique allows fabrication of such "solid-state liquid crystals" for different spectral ranges, from microwave to optical one. Full compatibility of used method with IC technology facilitates high-speed dynamic polarization control.

3 Fabrication of graphene shells

3D structures offer much promise as building blocks for nanoelectronic and nanomechanical devices, and for creating novel materials. To provide for electrical conduction of ultra-thin shells prepared from wide-band-gap semiconductor, modulation doping and surface passivation can be employed. Semimetals and many narrow-gap semiconductors possess sufficient conductivity. Among the latter materials, the most appropriate one is graphite, whose monoatomic layers- graphene display not only high electric conductivity, but also a number of unusual properties [22–24].

It was not long ago that monoatomic layers were believed to be nonexistent in a free state. The authors of [22, 24] showed that, using sequential multiple spalling, one can obtain micrometer-sized graphene islands on SiO_2. This technique proved to be suitable for preparation of separate samples. Yet, with this method, it is impossible to control the size and location of detached regions, and the substrate itself goes to waste as a result of the sequential multiple substrate thinning. The absence of an appropriate technology for mass production of graphene hampers the practical use of unusual properties of planar graphene layers. More then ten years ago it was shown possible to form, with the help of AFM tip, polygonal structures on highly oriented pyrolytic graphite (HOPG) surface by tearing and folding single graphitic sheets [25]. In this work we develop of a similar approach for fabrication of graphene shells. Such shells would substantially widen the functional capabilities of shell-based devices.

To prepare a free-standing graphene layer, we used a freshly cleaved HOPG surface obtained by peeling surface layers with a scotch tape. Normally, such a procedure yields a terraced HOPG surface with monoatomic steps. The present experiments were performed using a commercially available AFM microscope (NT-MDT, Solver-Pro, Russia). The surface was scanned in semicontact mode with 1 nm cantilever oscillation amplitude. For the experiments, cantilevers with high rigidity, of about 95 N/m, were chosen. First, we tried to find a most smooth region on the terraced surface of the sample with monoatomic steps. Then, the AFM microscope was changed over to contact mode, with the AFM probe pressed to the surface and subsequently displaced across the step edge in the direction normal to it as schematically shown in Fig. 3. As a result, the cantilever needle, encountering the edge of the monoatomic step,

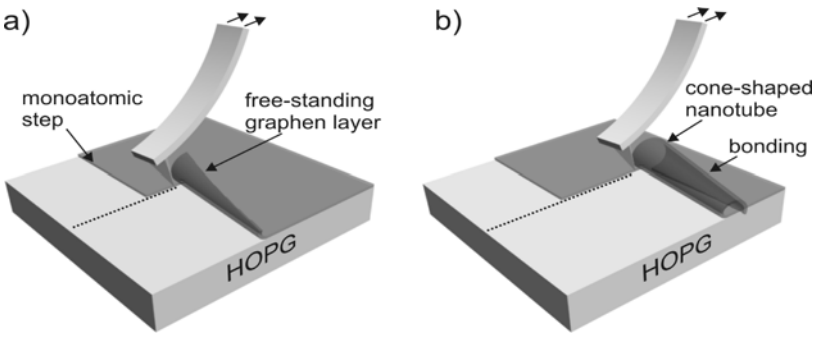

Fig. 3 Schematic illustrating the formation of a free-standing graphene layer on highly oriented pyrolytic graphite surface with the help of AFM probe.

detached a monoatomic graphen layer from the bulky HOPG sample (Fig. 3). Following this, the AFM microscope was transferred to semicontact mode to scan the surface once again.

Figure 4 shows two-dimensional topographic images taken from the areal part of the sample surface with monoatomic steps prior to and after the above procedure. Example illustrating the formation of free-standing graphene layers is the fabrication of a cone-shaped nanotube (see Fig. 4). Here the most likely manner in which the AFM probe lifts and folds the monolayer is that in Fig. 3. As soon as the edge of the free-standing folded film comes in contact with the surface, thus forming a full turn, Van der Waals bonding occurs, locking the formed shell in a stable configuration (Fig. 4b). In the region of immediate action of the probe a most imperfect zone seem to form. Along the step, the force that lifts the monolayer decreases with distance from the point acted upon by the probe; as a result, a closed monolayer shell forms, shaped as a cone. The height profile of the nanotube thus prepared, whose diameter at the cone vertex was about 0.8 nm. The lateral size of 50 nm is defined by the effect due to the probe shape. In our experiment, a ~400 × 400 nm^2 graphene layer was detached from the surface, subsequently locked in the folded state by Van der Waals forces.

We believe that, if further developed, the proposed nanostructuring method for local formation of shells from graphene layers will substantially extend the already existing possibilities in the formation of variously shaped graphene shells. Figure 5 exemplifies a periodic graphene corrugation obtained by scribing a flat surface of a graphite sample. In our opinion, the formed shell is stable here because, as a result of the force action, air molecules have penetrated in between the graphene layer and the bulky HOPG sample; these molecules prevented the graphene layer from returning into its initial flat state.

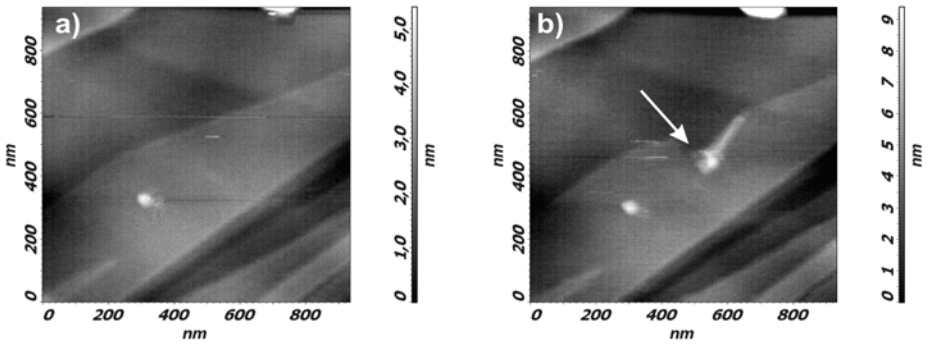

Fig. 4 Two-dimensional (2D) topographic images of the HOPG surface with monoatomic steps prior to (a) and after the detachment a graphene monolayer from the surface (b). The arrow indicates the initial position of the AFM probe and its moving direction. Here, the detached graphene layer has turned into a nanotube.

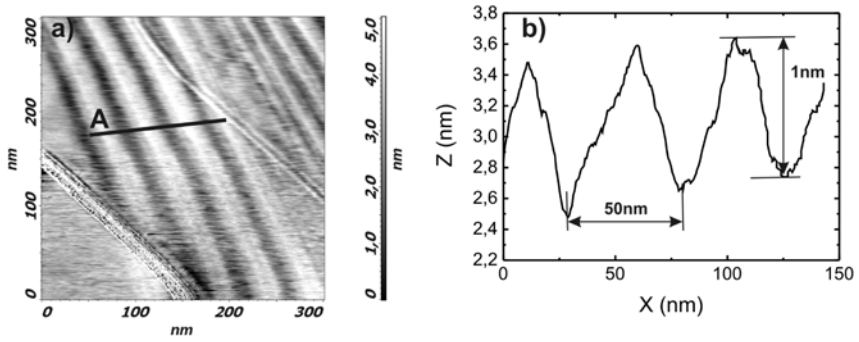

Fig. 5 a) AFM image of a corrugated graphen sheet, b) corrugation profile displaying a 1 nm corrugation amplitude.

Note that the formation of cylindrical, conical or just bent monoatomic shells is quite controllable a process, the latter being due to weak Van der Waals bonds between graphite layers. The resulting three-dimensional objects in the form of bent or rolled graphene have a number of obvious practical applications. One such example is an array of sharp-pointed cold emitters. In the formation of downcast contacts to bent or rolled grapheme layers, there arises a possibility to advantageously use the bent-layer effects, for instance, giant gradients of the surface-normal magnetic-field component and the related giant effects of magnetoresistance asymmetry [15].

In the formation of corrugated shells, we have a pronounced influence of still incompletely understood parameters such as the angle of AFM-probe inclination to the substrate surface. Such structures also seem to be promising in practical applications.

4 Conclusion

In conclusion, the fabricated semiconductor, semiconductor-metal and graphene shells provide a new generation of nanodevices and nanomaterials. Cone-shaped and corrugated graphite nanoshells have been fabricated.

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