

## Vapor phase synthesis of filamentary tungsten oxides by HFCVD

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The different macrostructures of filamentary tungsten oxides were produced by hot filament assisted chemical vapour deposition (HFCVD) using the ethanol as source of oxygen. The as-prepared products were characterized using scanning electron microscope, high-resolution transmission electron microscope and energy dispersive X-ray spectroscopy. A morphology of filamentary oxides varied from nanowires up to tubular microrods.  $\text{WO}_3$ ,  $\text{W}_{18}\text{O}_{49}$  and nonstoichiometric nanowires were found in the synthesized product. Moreover, the lead tungsten bronze nanowires with tetragonal crystal structure were obtained.

## Annealing and structural modifications of CN<sub>x</sub> nanofibers

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Carbon nanotubes and CN<sub>x</sub> nanofibers have significant potential for applications as field emission devices for flat panels and displays, as structural reinforcements for composites, as hydrogen storage cells etc. To improve properties of carbon nanomaterials, the purification of initial powder from metal-catalyst and amorphous carbon should be carried out.

CN<sub>x</sub> nanofibers have been obtained by means of resistive heating of graphite in a nitrogen gas environment of 25-40 MPa. The method of CN<sub>x</sub> -nanocarbons formation as well as their structure are presented in [1]. TGA and AES techniques have been used to investigate thermal stability and structural changes of the nanofibers during the following annealing in vacuum.

It was found that the nitrogen content does not change that indicates high thermal stability of C-N bonds. Vacuum annealing leads to a considerable mass loss due to the removal of impurities and defective carbon structures to healing of the structural defects of the nanofibers.

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## Transport properties of VO<sub>x</sub> multiwall nanotubes

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Vanadium oxide multiwall nanotubes (VO<sub>x</sub>-NTs) are considered as a new class of nanoscale magnets [1-3], which demonstrate a set of unusual magnetic properties including quantum critical behaviour [3]. At the same time little is known about transport properties and conductivity of VO<sub>x</sub>-NTs. In the present work we have studied VO<sub>x</sub>-NTs conductivity  $\sigma$  by comparison of the  $\sim 60$  GHz microwave response of the cavity loaded with the sample and the empty cavity [4]. The shift of the cavity resonance frequency and the change of the cavity quality factor were obtained as a function of temperature  $T$  in the range 4.2-80K and were used for the calculation of the  $\sigma(T)$  data (fig. 1). It is found that conductivity of VO<sub>x</sub>-NTs increases with temperature thus indicating on a dielectric type of transport. However the  $\sigma(T \rightarrow 0)$  tends to finite value rather than to zero (fig. 1).

The quantitative description of the observed  $\sigma(T)$  dependence may be obtained assuming presence of two contributions:  $\sigma(T) = \sigma_1(T) + \sigma_2(T)$ . The first term dominates at low temperatures  $T < 40$  K and is given by  $\sigma_1 = \sigma_0(T) + A \cdot T$  (fig. 1, curve 1), whereas the second term follows the Arrhenius law  $\sigma_2 \sim \exp(-E_a/T)$  (fig. 1, curve 2) with the activation energy  $E_a = (240 \pm 17)$  K. Basing on the comparative analysis of the microwave conductivity and magnetic properties [2,3] we suggest a possibility of the polaronic transport in VO<sub>x</sub>-NTs.

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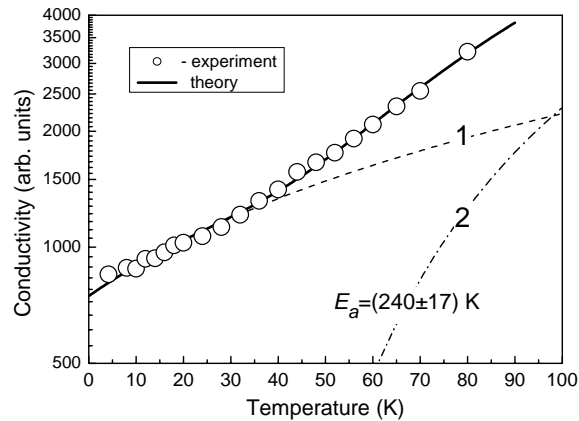


Fig. 1. Microwave conductivity of VO<sub>x</sub>-NTs at  $\sim 60$  GHz.

Support by the programmes of RAS “Strongly correlated electrons”, “Quantum physics of condensed matter” and by the RFBR grants 07-03-00749-a, 07-03-12182-ofi is acknowledged.

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## Beta-phase silicon nanowires: structure and properties

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The structure and properties of silicon nanowires under high pressure is almost a virgin field. Only in one work [1] a study of silicon nanowires (SiNW) in different phases was reported. The existence of silicon nanowires in new phases opens the new promising field in nanomaterial science due to they unique properties.

The electronic structure calculations of a set of silicon nanowires were carried out using density functional theory in the framework of local density approximation.

We studied SiNW in different directions truncated from the bulk silicon in  $\beta$ -Sn phase and compared them with corresponding wires truncated from the bulk silicon in  $\alpha$ -diamond phase.

To study the energetic stability, atomic structure and electronic properties of SiNWs the uniformly hydrogen-covered silicon nanowires were calculated.

We have examined the deviation of the Si-Si bond lengths from the bulk  $\beta$ -silicon bond length for each of the NWs.

The silicon nanowires binding energy dependence upon the effective diameter. Binding energy of wires in  $\alpha$ -diamond and  $\beta$ -Sn phases tends to the corresponding values of silicon crystal in  $\alpha$ -diamond and  $\beta$ -Sn phase, respectively.

We calculated SiNW phase transition pressure. This value lower than that observed in the bulk Si. This discrepancy can be explained by the misfit in strain energy of nanowires.

SiNWs in  $\alpha$ -diamond phase are more energetically favorable than SiNWs in  $\beta$ -Sn phase with nearly same effective diameter. The difference between wires in  $\beta$ -Sn phase of different orientations tends to zero with increasing of the wire size.

All examined SiNWs in  $\beta$ -Sn phase reveal metallic properties.

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## Formation of MoS<sub>2</sub> and Mo<sub>2</sub>S<sub>3</sub> layers on the surface of thermo expanded graphite

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Due to high thermal and electrical conductivity, as well as chemical and mechanical resistance, graphite materials are widely used as electrode materials, composite fillers, sorbents, etc. Formation of heterostructures based on graphite particles opens the possibility of creating materials with a wide range of functional properties. Graphite layers can be presented as a net from jointed carbon hexagons. Wide range of compounds, such as, for example, BN, MoS<sub>2</sub>, and WS<sub>2</sub> have the same structure. Commensurability of lattice parameters of graphite and the above-mentioned inorganic compounds allows creating nanocomposite structures in which the interaction between the components is provided by the Van der Waals forces. Thus, it has been demonstrated that surface of carbon nanotubes covered by MoS<sub>2</sub> and WS<sub>2</sub> layers [1, 2]

There are two stable crystalline phases of molybdenum sulfide: MoS<sub>2</sub> and Mo<sub>2</sub>S<sub>3</sub>; both have layered structure. MoS<sub>2</sub> particles are used in catalysis, as well as a lubricant. Mo<sub>2</sub>S<sub>3</sub>, thanks to the metal conductivity has perspective for application as a cathode material in lithium batteries. According to the phase diagram MoS<sub>2</sub> is stable up to temperatures ~ 2000K, and in the range from 937K to 2000K formation of Mo<sub>2</sub>S<sub>3</sub> is possible. Choosing the synthesis conditions, in particular, by altering the concentration of hydrogen, it is possible to obtain MoS<sub>2</sub> or Mo<sub>2</sub>S<sub>3</sub> nanorods. In addition, MoS<sub>2</sub> annealing in vacuum at 1300K results in the reconstruction of the surface with the formation of Mo<sub>2</sub>S<sub>3</sub>.

In the present work we present the results on formation of Mo<sub>2</sub>S<sub>3</sub> layers on the surface of thermo expanded graphite. We used the technique which previously has been used to form MoS<sub>2</sub> layers on the surface of the arc-synthesized multi-walled carbon nanotubes and other carbon-based nanomaterials [3]. As a result of experiments it is first shown formation of Mo<sub>2</sub>S<sub>3</sub> bi-layer on the surface of graphite. The reaction on the surface is faster than in the volume, since molybdenum (III) sulfide was not observed in the volume of the sample using X-ray diffraction and Raman scattering spectroscopy.

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## Theoretical investigation of the elastic properties of branched silicon nanowires

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Nanostructures, such as nanocrystals and nanowires (NW), represent the key building blocks for nanoscale science and technology. The nanowires are the most promising elements of the nanotechnology. They can be used as field-effect transistors (FETs), logic gates [1], and more. Another perspective technological field is to use the branched and hyperbranched nanowires. For example, the branched NWs might serve as building blocks to design 3D interconnected computing structure [2].

Presented here is a theoretical study of atomic structure and mechanical properties of the branched silicon nanowires of fork and bough types using model Tersoff interatomic potential. Using the extended cluster models, the effective Young elastic modules of the junctions were calculated.

Our simulations were performed using classical molecular dynamics, in which the Si-Si interactions were described by model Tersoff potential [3].

To simulate the external pressure we used the method of atomic plane [4].

Two possible types of three-terminal branched nanowires of finite lengths were studied. The first type (Y- "fork" configuration) has two equivalent branches attached to an end of the stem. This cluster was used to study the dendrite-like nanowires previously obtained in experiment [5].

We estimated the effective Young modulus of the Si-Y-NW junctions with two different diameters (17.3 Å and 13.4 Å). To study the effective Young modulus of the Y-shaped "bough"-type nanowires (Si-YB-NWs) we calculated composed nanowires with diameters 9.5 Å, 13.5 Å and 18.8 Å. To load the stress, the atomic plane was drove toward the single wire branch approaching the stem.

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## Origin of (-O-H) stretch mode in the chrysotile asbestos: neutron scattering and optical absorption study

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Interest on the physics and chemistry of nanomaterials has been stimulated by the results of theoretical and experimental studies of this field [1]. Nanowires or nanoparticles can be obtained by confining a solid or liquid within the nanometer pores of dielectrics matrix. Natural chrysotile asbestos (composition  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) is a regular set of closely pocked parallel ultrathin dielectric tubes with external diameter of 20-30 nm (this value determines the distance between the centers of the neighbor channels) and with internal channel diameter of 2-10 nm depending on the origin of mineral. The length of such object may be up to 2 cm and the total number of nanotubes is  $10^7$ - $10^{10}$  per sample. The chrysotile asbestos structure is described in detail by Whittaker using x-ray diffraction [2]. The aim of this paper is the study of origin of -O-H stretch mode by two methods: neutron scattering and optical absorption spectroscopy.

Unlike carbon nanotubes the chrysotile asbestos fibers form a microscopically aligned system of parallel nanoscale channels. It opens the opportunity to study the anisotropy of thermal vibrations in the directions along and perpendicular the channel axis using inelastic neutron scattering. Indeed the momentum transfer  $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$ , where  $\mathbf{k}_i$  and  $\mathbf{k}_f$  are wavevectors of incident and scattering neutrons, and in a case of  $\mathbf{k}_i \gg \mathbf{k}_f$   $\mathbf{Q}$  is antiparallel practically to the direction of an incident neutron beam. So having directed the channels along or perpendicular neutron beam we can study the vibrations along or perpendicular channel axis respectively. The typical spectra at 300 K for two possible orientations of  $\mathbf{Q}$  are presented in Fig.1.

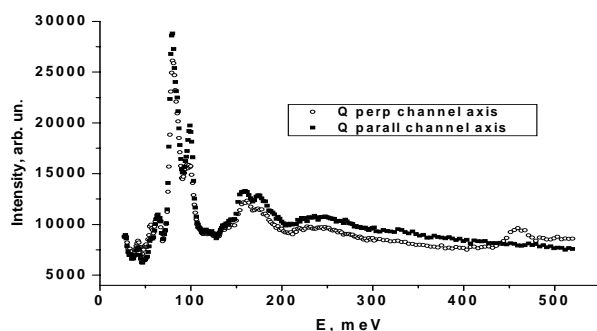


Figure 1. Spectra of thermal vibrations in chrysotile asbestos at 300K along (open circles) and across (black squares) the channel axis.

The principle difference between spectra is observed in the region 430-470 meV, where a high energy mode is stimulated. More likely this is the stretching mode of O-H groups, as according to the structure data these groups in asbestos orient perpendicular to the channel axis.

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## The theoretical prediction of new $\text{MgB}_2$ nanotubes

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The discovery of the carbon, BN, and dichalcogenide (Mo, W)S<sub>2</sub> nanotubes (NT) and the superconductivity of MgB<sub>2</sub> compound at 39 K [1] has led to the explosive activity of researchers in the field of study of inorganic magnesium diboride nanotubes. The existence of Mg<sub>g</sub>B<sub>2</sub> nanotubes and fullerenes has been predicted in [2]. Despite active theoretical activity in investigation of MgB<sub>2</sub> nanotubes, challenging questions regarding their energetic stability, stability, atomic structure and electronic properties are still open.

We systematically studied the energetic and the electronic structure of MgB<sub>2</sub> nanotubes with outer, inner and staggered configurations of magnesium atoms in the framework of the density-functional theory. It was shown that the energetic stability of MgB<sub>2</sub> tubes with outer and staggered magnesium layer displays minimum at certain diameters of the boron cage. We studied the influence of boron environment on energetic stability of MgB<sub>x</sub> nanotubes of different compositions like MgB<sub>3</sub>. Except narrow MgB<sub>2</sub>-NT with outer Mg arrangement, for which the structural tension opens the band gap, the MgB<sub>2</sub> nanotubes display metallic properties.

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## The investigation of growth mechanism of silicon nanowires

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Silicon nanowires (SiNWs), as a candidate material for nanoelectronic devices, are being intensively studied. Metal-assisted growth by CVD technique is a simple and efficient route for synthesizing controllable SiNWs at a low temperature. However, the metal-free growth is believed to have a potential for large-scale production [1]. The growth mechanisms, however, are still poorly understood under both circumstances. This study thus attempts to improve the understanding on the basis of the density function theory.

Here we investigated the mechanism of growing of the nanowires with small diameters from the silicon surface. We calculated the potential profile of adsorption of single silicon atoms on the surface on the different steps of growing of the wire.

We studied diffusion of the silicon atoms through the catalyst metal cluster. We calculated the energy barriers and found the values of the speed of diffusion of the atoms.

Also we studied the atomic structure and the electronic properties of the interface between the catalyst metal cluster and silicon surface/wire.

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## The theoretical study of electronic structure of single nanotube of TiB<sub>2</sub>

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In recent years, the number of works on the prediction or synthesis of new inorganic nanotubes has risen. A characteristic feature of all these tubular structures seems to be the existence of stable crystalline forms composed of a stacking of hexagonal layers, as graphite for carbon. This structural particularity can then serve as a guide for the search of new tubes with specific properties and applicabilities.

The crystalline form of titanium diboride (TiB<sub>2</sub>) has a P6/mmm space group symmetry, consisting of the stacking of alternate hexagonal boron and triangular titanium sheets. Among other interesting properties, TiB<sub>2</sub> presents an attractive combination of mechanical, chemical and transport properties such as high hardness, low electrical resistivity, good thermal conductivity and chemical inertness [1], which turns this material an excellent candidate for several applications.

The TiB<sub>2</sub> nanotubes should inherit the attractive properties of the precursor crystal. Recently [2], it was shown, that the TiB<sub>2</sub> nanotubes can be used for hydrogen storage with capacity up to 5.5wt.% However a systematical study of the structure and properties wasn't carried out.

In this work, the series of TiB<sub>2</sub> nanotubes of different types and chiralities have been studied.

*Ab initio* calculations of the binding energy, the electronic band structure, the density of states, the dependence of the strain energy of the nanotube on the nanotube diameter for TiB<sub>2</sub> nanotubes of different diameters are performed in the framework of the density functional theory.

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## The adsorption properties of boron nanotubes

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At the moment active search of new surface structures capable of effective adsorption of different gases (including hydrogen) is being carried out. That gives new opportunities in energy industry development. We have investigated an binding opportunity between the atoms of hydrogen, fluorine, chlorine, oxygen and the outer surface of single-walled boron nanotube of (6,6) type and have studied the mechanism of this process. The calculations are carried out within the model of molecular cluster with the use of quantum chemical MNDO scheme [1].

Three variants of adatoms' orientation over the tube surface were considered: I) over boron atom, II) over the centre of B-B bond, III) over hexagon centre. Surface patterns of potential energy for these processes were built. The analysis of curves showed that all atoms are adsorbed on the surface of B-tube. Adsorption distances ( $R_{ad}$ ) and adsorption energy ( $E_{ad}$ ) were calculated for all selected atoms. Adsorption processes for options II and III were simulated in a similar manner. It turned out that adsorption of H and O atoms is implemented only for option II, and adsorption of H atom – for option III.

Regular hydrogenation of boron nanotubes was investigated. Calculations of two variants of hydrogen atoms binding to the outer surface of nanotube were carried out: 1) H atoms are arranged over B atoms of three adjacent hexagon layers (six H atoms over each layer) so that rings of superlattice formed by adatoms are not displaced relatively each other; 2) even ring of adatoms are displaced as for uneven at the length of B-B bond. The difference of full energies of these options is  $\Delta E = 4 \text{ eV}$ , the second option of hydride boron nanotube structure turned out to be energetically more favourable.

So we can confirm that generation of gas-phase hydrogen composite materials based on boron nanotube is possible.

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## Semiempirical investigation of boron nanotubes and some structure-modification composites on its base

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The problem of formation possibility nanotubular structures for group of substances which can form layered crystals, is actively discussed now. We assumed that boron is the nearest neighbour of carbon and it can make quasiplanar hexagonal form similar to structure of graphite. That's why it is possible to assume the possibility of boron nanotubes formation.

We considered the fragments of single-wall boron nanotubes (n, n) type (n = 4, 5, 6, 9, 11, 12). Calculations were carried out by IB-CCC method [1]. The analysis of band-gap  $\Delta E_g$  showed that all of them are semiconductors, independent of diameter. Energy of deformation was calculated as a difference of quasiplanar extended unit cell (EUC) energy and energy of boron nanotube which made of corresponding EUC. We defined that energy of deformation decreases with increase of the diameter of boron tubes (n, n) type. The charge analysis of boron tubes has established that their symmetry is stable (charges on boron atoms are almost equal to zero).

Also we considered the fragments of single-wall boron nanotubes (n, 0) type (n = 4, 5, 6, 8, 12). In this case energy of deformation is increases with increase of the diameter of boron tubes (n, 0) type. So, we can conclude that formation processes of «zig-zag» boron nanotube from flat hexagonal boron structure energetically isn't useful and possible.

Calculations of boron nanotubes (6, 6) which contained various defects of structure (structure-modification B-tubulenes) were obtained by the quantum-chemical semiempirical computational MNDO scheme. We research substitution imperfection of boron atom by carbon atom (C), positive carbon ion ( $C^+$ ) and negative carbon ion ( $C^-$ ). We found out substitution energy of defects and their atomic energy level. We studied the boron nanotube with hole and determined the energy of defect activation and the relative portion of vacancies.

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