Impact of 1D nanocrystals grown in the channels of SWNTs on electronic properties of obtained nanostructures

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Single-walled carbon nanotubes (SWNTs) first produced in 1991 nowadays draw close attention of scientific community worldwide due to their unique electronic and structural properties accompanied by extraordinary mechanical behavior depending on the diameter and conformation of tubes. The filling of SWNTs with favourable conductive, optical or magnetic materials impulses the development of novel class of nanotube architectures and nanoscale materials. This approach allows us the tuning of electronic structure and properties of SWNTs and enabling their great potential applications as active elements of electronic devices and circuits.

The present study is focused on the controllable growth of 1D nanocrystals (CuI, AgI, S, Se, Te, CdS, PbS, ZnS) in channels of single-walled carbon nanotubes with inner diameter 1-1.4 nm and investigation of their effect on electronic properties of obtained nanostructures. The synthetic strategy is based on the impregnation of pre-opened SWNTs by molten salts in vacuum using capillary forces.

The structure of 1D crystals formed in SWNTs is characterized by HRTEM imaging and EDX analysis, proving the successful filling of nanotube channels with one-dimensional nanocrystals of chosen materials. It is shown that incorporated compounds affect the electronic structure of SWNT resulting in the shift of RBM- and G-lines of Raman spectra, corresponding to the shift of the Fermi level of nanocomposites.

Besides, it was shown the possibility of carrying out the chemical reaction in channels of single-walled carbon nanotubes in terms of nanostructures CdS, PbS, ZnS/SWNTs for the first time.

Polymerization of the Ñ$_{60}$ fullerene films with their alloying with the copper and titanium atoms

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Alloying with alkali metals, in particular by rubidium and potassium, of the C_{60} fullerene films leads to the essential transformation of their electronic and vibrational structure. The changes indicated are caused by the polymerization of C_{60} molecules, although in contrast to photopolymerization, which is accomplished due to [2, *2] cycloconnecting, the mechanism of polymerization with the alloying is studied not sufficiently. It is obvious, that as a result of the ionization of the components of "metal-fullerene" system, and also the hybridization of their electronic states, it is possible the most essential transformation of their energy structure.

With the doping by alkali metals the transfer of external electrons from the atoms plays the determining role, to what contributes the high energy of an affinity of C_{60} molecules to the electrons. The role of the hybridization of energy states proves to be insignificant. The obtained result cannot apply to all metals, taking into account the differences in their electron structure.

Film "metal -fullerene" samples were selected for studying the polymerizations of C_{60} fullerites during their intercalation. They were created with the joint vacuum condensation of the metal atoms and C_{60} molecules on the silicon support during their evaporation from two sources, which contain heating elements. The concentration of components was regulated by the evaporation rate of the metal atoms. Two types of samples were used, mainly, Cu-C_{60} and Ti-C_{60}. The content of the metal atoms was from 1 to 50 atoms to one C_{60} molecule.

The electronic structure of these films was investigated by the spectral ellipsometry method with the study of interband transitions. Changes in the crystalline phase with the alloying were determined by the X-ray diffractometry method.

It is shown, that the electronic spectra with the alloying by the copper and titanium atoms essentially differ, indicating, that in the case of doping by titanium atoms not only the ionization plays the important role, and also the hybridization of energy states. In particular, with an increase in the titanium atom concentration the influence of the hybridization of electronic states on the polymerization sharply grows. This testifies about the difference in the mechanisms of polymerization, which are observed in the studied systems.

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The features of C_{60} films evaporation

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In the present work results focused on the investigation of the pure C_{60} films evaporation process are reported. The evaporation velocity has been experimentally measured and the values of the fullerite saturated steams pressures in the temperature range (250–290)°C are obtained. It is established, that the temperature dependence of the evaporation velocity is displaced toward the low temperatures approximately by 100°C, and the pressure of the saturated steams is essentially higher than the tabular values. The atmospheric oxygen and the ultraviolet irradiation influences on the fullerene evaporation parameters are studied. It has been shown, that affected by the external environment factors, on the surface of the fullerite the thermo-stable oxy-polymeric layer, acting like a diffusive barrier, is formed. This leads to the essentially decrease of the C_{60} evaporation velocity.

Clustering in amorphous carbon films probed by the charge transport and structural studies

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Amorphous carbon films are known as materials whose properties are determined by their cluster structure. In the present work the influence of the deposition energy on the carbon phase structure and charge transport in hydrogenated amorphous carbon films containing silicon and oxygen is studied. The carbon nanocluster films were grown on the polycrystalline dielectric substrates by PCVD of the vapors of heavy silicon-organic polymer $((CH_3)_3SiO(CH_3C_6H_5SiO)_3Si(CH_3)_3)$ in DC stimulated discharge. The energy of deposition was proportional to the self-bias potential V_{SB} appeared on the RF (1.76 MHz) powered substrate holder. The conductivity of the films was measured in the temperature range from 80 to 400K and in applied electric fields up to $E = 7 \bullet 10^5$ V/cm. The carbon phase structure was probed by Raman spectroscopy. The study of the electron transport has revealed that for the electric field $E < 2 \bullet 10^4$ V/cm in the entire range of V_{SB}= -100 ? -1400 V the obtained data may be adequately described by hopping conductivity in the exponentially distributed bandtails of the localized states, assuming that the transport energy level is positioned above the Fermi level [1]. It is found that DOS at the Fermi level $N(E_F)$ demonstrates a non-monotonous dependence on V_{SB} (Fig.1). On the basis of Raman spectroscopy data we argue that the enhancement of $N(E_F)$ is caused by the growth of the sp^2 coordinated carbon nanoclusters whereas the nature of the broad maximum at V_{SB}~-600 V requires further investigations. Application of the electric field exceeding $E \sim 2 \bullet 10^4$ V/cm induces a drastic change in the charge transport mechanism: the conductivity becomes non-ohmic and is controlled by the phonon-assisted or direct tunneling on the mobility threshold. The role of the carbon nanocluster in the latter process is discussed. Support from the program of RAS "Quantum macrophysics" is acknowledged.

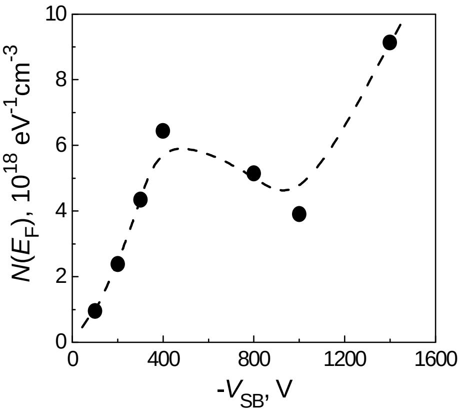

Figure 1

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On the role of polarization in formation of new carbon modifications: fullerenes and nanotubes

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The role of polarization of graphene fragments by positively charged ions of inert gases or transition metals in the mechanism of formation of curved carbon modifications is discussed. It is assumed that positively charged ions play the role of a catalyst in the process of curving of a graphene layer and nucleation of fullerenes and nanotubes. This is a new mechanism of catalysis which has not been discussed before because it was believed that the electron polarizability of an atom cannot affect its reactivity.

A graphene fragment surrounded by π-electron clouds from two sides exhibits, however, a very high polarizability, and the configuration of its electron clouds can appreciably change under polarization. Since the flatness of graphene is due to equivalence of its electron clouds and, first of all, equality of π-electron densities, the redistribution of π electrons between two sides of a carbon frame of graphene must give rise to curving. Numerical estimates of the angle of polarization-induced curvature of a graphene fragment consisting of two carbon hexagons based on a simple model of electrostatic repulsion of π electrons and taking into account rigidity of carbon bonds obtained from the data for CO_2 give the value of the two-dihedral angle close to its value for fullerenes (156° and 137°, respectively). An important feature of such a mechanism of curving of graphene fragments is fixation of the π-electron redistribution after the polarization is stopped. The fixation is achieved by formation of a π bond with a multiplicity equal to 1. The suggested mechanism of formation of new carbon modifications allows one to understand the difference between the conditions of formation of fullerenes and nanotubes and also the conditions of graphene polarization determining the chirality of nanotubes.

The point symmetry monoelement nanoparticles

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At the XX century the new matters were discovered. The first of all they are quasicrystals and fullerenes. These objects have 5- and 10-axis symmetry which is forbidden for crystals. The 3×3 matrices-generators of point groups of rotation in crystallographical and crystallophisics basises have as matrical elements 0 or ±1 (except groups hexa- and trigonal in H-basis crystals). For groups with 5 along z-axis in orthogonal basis matrix-generator (M_5) is

$$\mathrm{M}_5 = \begin{pmatrix} \frac{\tau}{2} & \frac{\sqrt{\tau+3}}{2} & 0 \\ -\frac{\sqrt{\tau+3}}{2} & \frac{\tau}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

where $\tau = (1+\sqrt{5})/2$ is a golden ratio. For description of point groups penta- and decagonal symmetries it is necessary instead of crystal lattices take is named general regular lattices (GRL). The two dimensional GRL is known as Penrose's sets. For 3-d pentagonal sets there are 14 groups of point symmetry which are not crystallographic because their elements may be golden ratio [1]. For instance group with 5-order axis in GRL is next

$$\begin{pmatrix} 0 & 0 & 1 \\ \tau & 0 & -\tau \\ 0 & 1 & \tau \end{pmatrix}, \begin{pmatrix} 0 & 1 & \tau \\ 0 & -\tau & -\tau \\ 1 & \tau & 1 \end{pmatrix}, \begin{pmatrix} 1 & \tau & 1 \\ -\tau & -\tau & 0 \\ \tau & 1 & 0 \end{pmatrix}, \begin{pmatrix} \tau & 1 & 0 \\ -\tau & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

In 3-d space there are five different GRL with maximum group of point symmetry m5m. It has order 120. Gram's matrices [1] these lattices are next

$$\begin{pmatrix} 2 & \tau & 1 \\ \tau & 2 & \tau \\ 1 & \tau & 2 \end{pmatrix}, \begin{pmatrix} 3-\tau & \tau & \tau-1 \\ \tau & 3 & \tau \\ \tau-1 & \tau & 3-\tau \end{pmatrix}, \begin{pmatrix} 2 & 1-\tau & 1-\tau \\ 1-\tau & 2 & 1-\tau \\ 1-\tau & 1-\tau & 2 \end{pmatrix}, \begin{pmatrix} 5 & 2\tau-1 & 2\tau-1 \\ 2\tau-1 & 5 & 2\tau-1 \\ 2\tau-1 & 2\tau-1 & 5 \end{pmatrix}, \begin{pmatrix} 3 & 1 & 1 \\ 1 & 3 & 1 \\ 1 & 1 & 3 \end{pmatrix}.$$

The m5m point group has some noncrystallographic subgroups. They are

$$m5m\,(120),\quad 532\,(60),\quad \overline{10}m2\,(20),\quad 5m\,(10),\quad 52\,(10),\quad \overline{10}\,(10),\quad 5\,(5).$$

The orders of groups are in parentheses. Point group with maximum decagonal symmetry is $10/\mathrm{mmm}$. Its order is equal 40, and it has the noncrystallographic subgroups:

$$10/mmm\,(40),\quad 10mm\,(20),\quad \bar{5}2m\,(20),\quad 10.22\,(20),\quad 10/m\,(20),\quad 10\,(10),\quad \bar{5}\,(10).$$

It was shown that quasicrystals, fullerenes and nanocrystals may be described by theory of regular generalized lattices.

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The size bound between nano- and macrostate

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Now the nanoparticles (NP) are naimed the particles of matter with size not more then 100 nm. But it is known that nanoproperties depend on the nature of matter. It means the influence of the crystal chemistry properties of bulk state (BS) matter from which nanoparticle was made to size bound between NP and BS. It may think that for evaluation of this size bound (L_0) it needs take the simple method for calculation of this parameter and this method must takes account of standard physical constants. In physics there is temperature boundary witch divides the quantum and classic approximations for description of crystals. It is Debye's temperature (θ_D).

If $T > \theta_D$ then physical phenomena are described by classic physics methods otherwise it must take quantum ones. Side by side with Debye's energy $(E_D = k\,\theta_D)$ it is proposed to use Debye's impulse (P_D) for electrons in the particles. After this we must take uncertainty relation: $(P_D)_i \cdot (L_0) = h,$ where i=x, y, z. But $P_D = \sqrt{2E_D\, m_0} = (P_D)_i \cdot \sqrt{3}.$ Hence it follows

$$L_0 = h\sqrt{3}(2m_0\,k)^{-1/2}\theta^{-1/2}, \tag{1}$$

h, k are Plank's and Boltzmann's constants, m_0 is mass of electron.

Consequently $L_0 = 230 \cdot \theta^{-1/2}$ [nm]. The L_0 are maximum value for nanosizes of particles when they are different from balk matters. F.e. for diamond $L_0 = 5\,nm$ $(\theta_D = 1850\,K)$ and for lead $L_n = 24\,nm$ $(\theta = 95\,K)$. Value L_0 is a size bound when mechanism of physical processes changes. If R is particle size and $R > L_0$ then the size of particle does not influence to mechanism of physical processes and this matter is macro- or bulk ones. When $R < L_0$ then the properties (N) of particles different from properties of the bulk objects and depend on the size of NP. In general case the function N(R) may be written as

$$N(R) = N_0 \left| \exp\left(- \sqrt{\frac{L_0}{R} - 1} \right) \right|, \tag{2}$$

where N_0 is BS – properties.

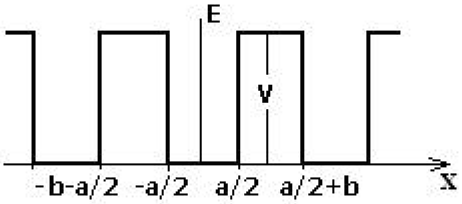

Fig. 1. Periodic potential field.

The formula (1) is deduced also from describing of electron energy state in the crystal. Indeed let electron is found in the periodic potential field $u(x)$ (fig. 1). Parameters a and b are the widthes of potential pits and barriers accordingly. With consideration of potential field period (T=a+b) the solution of Schrodinger's equation for the electron in the first pit is

$$\psi'(x \pm nT) = \exp iknT \cdot \psi(x) = u(nT)\psi(x), \tag{3}$$

n – integer number. If $(unT)_{\max} = 2\pi$, then $E_{\max} = \dfrac{h^2}{2m(L_r)^2}$. If $E_{\max} = E_D$ then result formula for calculation L_0 is the same as (1).

Simulation of CNT modification by ion bombarding

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One of the most perspective and attractive problems of modern physics and technology is the studying and practical using of carbon nanotubes. An unsolved problem of the technology is creation of nanotubes with prescribed sizes. Tubes of the given diameter can be created by setting adjustable synthesis parameters, but their length can reach microscopic sizes and still remains an uncontrollable parameter. The purpose of this report is to study interaction of ions beam with a SWCNT with aim to create a basis of technology for their cutting.

Interaction of a swift charged ion with SWCNT can be conventionally parted into three stages [1]: 1) transferring of the ion energy to tube's nuclear and electronic subsystems; 2) relaxation of the excited electronic subsystem together with 3) the nuclear one. The first stage was treated in details. It was studied within framework of the binary encounters approach and correlations of elastic and inelastic events have been made by the following semi-classical model: 1) particle's trajectories are calculated with account of electronic state of them and electronic stopping; 2) electronic stopping is calculated with account of the trajectories [2]; 3) the linked equations are solved in zero and first approximations on the correlations values.

Irradiation of SWCNT(10,0) by C^+ ions with energy 1-50 keV has been modelled. Interaction potentials with different screening, polarization, exchange and correlation, and charge of partners were examined for study of the effect scale. Similarly, the atom electrons density and their average velocity were varied in the electronic stopping. It was found, that near the energy, where electronic and nuclear stopping are close each to other in zero approach (about $E \approx 10$ keV), the values of first order corrections can reach about 10% of zero approximation ones depending on interaction. But, the cross section of elastic scattering can change much more due to charge variations. Therefore, more significant influence could have the correlations of nuclear scattering and electronic stopping in consecutive collisions of two ions with the same atom, if it has been ionized by the first ion and did not been neutralized before the second collision. Such conditions can be achieved at high current density of a focused ions beam, or in a molecular ions beam, and should be taken into account in simulation of these processes.

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The role of secondury electrons in forming the image of electron nano-probe

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Electron-beam lithography is known to be a widely spread technique in microelectronics. There are already a lot of examples of using fullerite C_{60} films in the technique as a negative electron-beam resist characterized by extremely small (1 nm) sensitive grain. Unfortunately, neither this advantage nor nano-size scale (~3.5 nm) of the modern nano-probes are not result in the possibility of formation of nano-images because of scattering of the primary diagnostic electrons and expanding nano-probe. We report hear one more mechanism of widening the image of electron nano-probe: the mechanism of formation of the image of secondary electrons which fill much larger area than scatted ones and form larger pixel. Manifestation of this mechanism is seen in the photo of carbon clusters created by electron nano-probe in fullerite film. The film was irradiated in certain points by electron nano-probe with diameter being less than d~10 nm and developed in chlorbenzene. Irradiation of the film and visualization of the sample were made by Scanning Electron Microscope- JEOL JSM-6380LA. Two bright spots in the figure are carbon clusters created by the primary and scatted electrons. Their radius is of about 60 nm. The clusters are superimposed on the larger clusters with the radius of about 500 nm which were created by a swarm of secondary electrons. Diminution of the exposure dose results in disappearance of the supporting clusters because of decreasing the density of secondary electrons below the critical level. Current and time derived dose dependences of the cluster size were revealed to be different in the revealed mechanism because of the diffusion character of spreading the secondary electrons. Computer simulation of the process was performed. It confirms the experimental results. The conclusion was made that the revealed mechanism should play an important role in the case of the dense lithographic pictures.

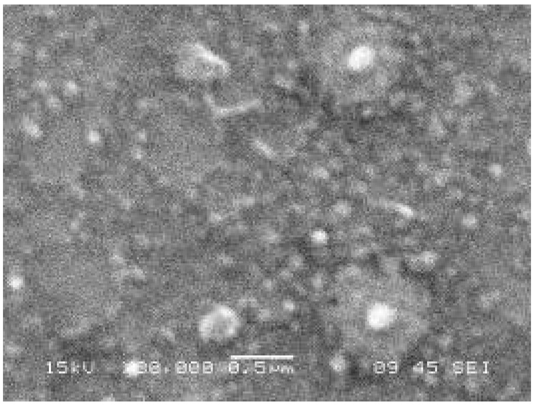

Fig.1. A Scanning Electron Microscope photo of carbon clusters created by electron nano-probe in fullerite C_{60} film.

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The thermodynamic properties of amorphous carbon nanostructures synthesized by HPHT treatment of C_{60} fullerite

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In the present work by methods of precision adiabatic vacuum and differential scanning calorimetry in the range from 6 to 650K the temperature dependences of heat capacities $\tilde{N}_{ð}^{\circ} = f(T)$ of amorphous carbon nanostructures were studied. The tested samples has been synthesized by high pressure-high temperature (HPHT) treatment of *f.c.c.* C_{60} fullerite at $\grave{O} = 1373$K and $p = 2$ and 8 GPa. The low-temperature heat capacity ($20 \leq \grave{O} \leq 50$K) was analyzed on the basis of Debye theory of heat capacity of solids and its multifractal variant that allowed the conclusions about the heterodynamics character of structure of the studied substances. On obtained experimental values the standard thermodynamic functions, namely, the heat capacity $C_p^{o}(\grave{O})$, enthalpy $H^{o}(T)-H^{o}(0)$, entropy $S^{o}(T)$ and Gibbs function $G^{o}(T)-H^{o}(0)$ were calculated for the range from $T \to 0$ to 650K as well as standard entropies of formation nanostructures from graphite, diamond and *f.c.c.* C_{60} fullerite at $\grave{O} = 298.15$K were estimated. The comparison of standard thermodynamic characteristics of studied amorphous carbon nanostructures and some allotropic carbon modifications was carried and as results the HPHT effects on its physicochemical properties was determined.

The work was performed with the financial support of the Russian Foundation of Basic Research (project No. 05-03-32363), FCNTP Program (St. Contr. No. 02.442.11.7486).

Electrical characterization of nanoscale Pt structures deposited using Focused Ion Beam

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Dual Beam FIB-SEM (focused ion beam – scanning electron microscope) system (Nanolab 200 of FEI) was used for deposition of thin films of Pt (thickness in the range of 5-300 nm) on thermally oxidized Si. One of the important applications of FIB-deposited Pt structures is formation of nanocontacts for electrical characterization of nanostructured materials. Both Ga^+ ion and electron beams can be used for the metal deposition. The composition (C, Ga and O impurities), resistivity of FIB-deposited Pt patterns and the quality of contacts depend on the deposition parameters and film thickness. Various test patterns (squares and lines) were deposited for electrical characterization of the films, using 2 and 4 points techniques. Tests with parallel Pt lines were also carried out, and considerable leakage (“due to the “halo” effect) was detected for the interline distances in the sub-micron range. The leakage was shown to depend strongly on the quality of the substrate. For rougher surfaces, lower leakage currents were measured. Surface roughness was introduced by short time exposure to the ion beam. Comparison between electron and ion beam deposited films will be also reported.

On the hydrogen intercalation with carbonaceous nanostructures and the spillover enhancement: relevance to solving the on-board storage problem

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The thermodynamic analysis (2003-2006) of the indirect experimental character, some re-treatment and systematization is performed with respect to the most significant data (1999-2006) on the hydrogen sorption by graphite and related carbon-based nanomaterials (single-walled and multi-walled nanotubes (SWNT, MWNT), fullerenes, graphite nanofibers (GNF), nanostructured graphites) at technological temperatures and pressures.

The indirect experimental values of the thermodynamic, kinetic and diffusion fundamental characteristics of sorption processes (both the chemisorption and physisorption ones) are refined and compared with the theoretical quantities and models, for revealing of the micromescanisms and technological optimizing of the interaction between hydrogen and carbon materials.

The attention is concentrated on the Rodriguez-Baker series (1995-1999) of the unique, non-reproduced studies of GNFs, where a "super" hydrogen adsorption capacity (H/C ? 6-8, at 11 MPa) has been declared. As analysis has shown, a considerable part of data on the thermo-desorption characteristics of ~30% of the total capacity (the residual hydrogen) is in a satisfactory accordance with other known related data on the chemisorption, particularly, with data (1999-2003) on the mechanical synthesis of hydrogen with graphite (at 1 MPa) and data (2004) on GNFs and SWNT bundles (charging at 9 GPa). As has also shown, the local concentrations of the residual (chemisorped) hydrogen in GNFs (after a fast release from them of ~70% of the total amount of H/C ? 6-8) are of the "carbohydride-like" values (H/C ? 0.5-1).

The anomalous (fast released) amount of the adsorbed hydrogen (~70% of the total capacity of H/C ? 6-8) in GNFs can be related to a poly-layer physical adsorption (as an unusual condensation and/or intercalation) induced by chemisorption. It is consistent, for example, with data (2004) on the dehydrogenation behaviour (the microstructure nanofragmentation) of GNFs, with data (1999) on a separation of the individual SWNTs under the hydrogenation, and theoretical data (2005) on developing "tuneable" graphite nanostructures, which are some development of the Dubinin concept. It is also consistent with data (2004-2006) on the spillover enhancement (of about an order of magnitude) of the hydrogen storage in carbon materials, and especially, with conclusion (2006) on the intercalation vs. chemisorption mechanisms, and emphasizing (2006) on the renewed interest to carbonaceous nanostructures relevance to the on-board storage problem. As has stated in literature, the enhancement mechanisms are not well understood and further studies are necessary.

Analysis has shown that the spillover enhancement cannot have place for the physisorption mechanisms in principle, unlike to the dissociative-associative (physi-like) chemisorption ones. The effect can be related with the above noted concept on the hydrogen intercalation induced (initiated) by the chemisorption.

Finally, it is concluded that there is a real possibility of developing the carbonaceous "super" adsorbents of hydrogen for the vehicular and other applications, and that the further studies of the hydrogen intercalation with carbonaceous nanostructures is a real way of solving the on-board storage problem for the fuel-cell-powered vehicles.

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Composites on basis Fe with additives nanocarbon materials

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Authors spent works in a direction of creation of new constructional materials on basis Fe-C with use nanotechnology and nanocarbon materials.

Samples prepared from powders carbonyl iron and a row nanocarbon materials (fullerene containing soot, fullerenes, nanotubes, nanofibers, nanodiamonds) in the ratio Fe-3-5-10 weights of % C (17 variants mix materials have been made).

As a result of high-temperature, intensive plastic deformation in samples the structural state is established unusual for Fe-C materials. In each of samples it especial on structure and properties. Formation of a superhard phase with microhardness >30 GPa is revealed. Such phase is contained with all samples. The sizes, the form and quantity of a superhard phase are various. Microhardness of other phases is within the limits of 5-11 GPa. By X-ray spectrum microanalysis it is established, that the superhard phase contains only carbon. The X-ray diffraction phase analysis determines presence in samples of various quantities of a superhard phase (it is determined on crystallographic to parameters of the patent [1]), α- and γ-Fe, fullerenes C_{60}, C_{70}, and carbides iron. α-Fe all samples has nanostructure a state - the size of blocks ~10 nm.

The analysis of structural state Fe-C composites samples has allowed to draw a conclusion, that contained in initial nanocarbon materials graphite participates in formation carbides and is dissolved in Fe. Amorphous carbon, nanotubes, nanofibers and fullerenes - i.e. all nanocrystal carbon are a basis of formation of the various form and dispersiveness superhard phase. The proof of it is reception of samples with a superhard phase and without fullerenes.

Possible scopes of the received composite materials - use as constructional, tool and materials for work in conditions of friction and wear.

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The method for inertialess controlled doped or multilayer metal-fullerene films growth

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Since the discovery of effective fullerene synthesis and isolation methods [1] they became available for different research works. One of the first direction was related with thin fullerene films growth. Reserchers expected to get films for creation uniqe property superconductors, sensors, optical gates and other devices. Unfortunatly too few things were realized. By nowadays the great practical experience have shown that fullerene remains perspective material for solving these tasks. Most of the faults were made because of unaplicability of existing equipment for pure fullerene and doped fullerene films growth.

Due to the difficulties in providing stability and repeatability of the growth behaviour resistive heating used in the most setups is not suitable for fullerenes. Fullerenes evaporate slowly under temperature of 480°C but they evaporate avalanche-like if temperature exceeds this barrier by just a few degrees. Under the slow sublimation conditions, the growing film has crystal structure, and under the fast sublimation conditions, it has amorphous structure containing crystals of source powder. In both cases, fullerenes are condensed into clusters, which do not allow growing films with expected properties.

Thermovacuum method with inductive heating, used in our installation, has allowed us to localize heating area directly near the evaporating material and to remove heating from both vacuum chamber and substrate. Evaporated material has been placed on the bowl’s surface, heated by Fuko currents, induced by alternate magnetic field of inductor. The alternate current generator has supplied power for inductor at the 66 kHz frequency. Every bowl temperature measurements have been carried out by thermocouples under the computer control of the film growth behavior. We have modified vacuum post VUP-5 and have developed the method for growth of uniform fullerene films, doped by churlish metals, such as tungsten and molybdenum.

The properties of obtained films depend on both material, sputtered on the substrate’s surface, and structure of this material, forming at the growth process. Usually fullerene deposition on substrate occur in form of clusters, consisting of 10 to 100 molecules, however in order to obtain smooth and uniform structure it is necessary to provide single molecule sputtering. In our work, we suggest to irradiate fullerene clusters by electron beam, charging clusters with the help of electron gun, placed inside vacuum chamber. It is possible to get epitaxial fullerene films in this case.

Inputting into the chamber two inductors allows implementing simultaneous, non-inertial evaporation of fullerenes and doping material.

Fullerenes and doping materials evaporated from different bowls for the best control of growth behavior of doped and multilayer fullerene films. The temperature of every bowl was measured by individual thermocouple and the computer controlled heating according to the program. The film was placed under the common stream or consequently moved from one bowl to another. It depended on selected film type – doped or multilayer. The developed setup implemented as a block for controlled thermal film growth, can be combined with any vacuum post and allows essential reducing of thermal inertia at doped and multilayer metal-fullerene films growth with high repeatability.

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Dynamics of multiple-charged fullerene ion fragmentation

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Fragmentation of fullerene ion formed due to loss of several electrons captured from fullerene molecule by incident multicharged ion of kev-energy was studied experimentally. The charge of initial fullerene ion was determined using charge change analysis of the incident ion after its collision with fullerene molecule. The mass spectra of fullerene fragment ions were determined from their time-of-flight in TOF analyzer. The kinetic energy spectra of each of definite mass of fragments and correct ratios between their intensities were calculated from shape of lines in the mass-spectra. The data obtained for simplest case of molecular ion fragmentation when two protons are formed at two-electron capture from hydrogen molecule[1] were used for testing and calibration of experimental system and calculation method.

As it is known stable multiple-charged fullerene ions can exist up to charges at least 9 (see for example [2]). But is was found that at collision of fullerene with multiple charged ion the loss of four and more electrons leads to formation of corresponding number of singly charged fragment ions and some amount of neutral fragments. This means that the potential energy transferred to forming fullerene ion is enough to break off many interatomic bonds. As a result the fullerene ion fragmentation occurs as a Coulomb explosion.

The dynamics of fullerene multicharged ion fragmentation was analysed. Because of spherical symmetry of fullerene ion there should exist an accurate connection between fragment-ion energy and mass at one-stepped dissociation. The observed kinetic energies of main part of C_2^+ ions and more heavy ions correspond to this one-step process. But some deviation from this connection was found for part of ions for all mass fragments. The energies of most of C^+ fragment-ion gives evidence of the existence of more complex two- or more-stepped formation process of these ions.

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Unconventional polymorphic modifications of carbon and boron nitride: existence, structure, electronic properties and bulk modula

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Structures of unconventional polymorphic modifications of carbon and BN predicted theoretically and synthesized experimantaly were analysed critically, including amorphous and metallic carbon, C8, carbyns, nanotubular crystals, “cubic graphite”, graphanes, chaoite and other nanostructures. Number of the structures is suggested to design from especial crystalcreated fullerenes $\tilde{N}_n$ and fulborenes $B_{n/2}N_{n/2}$, n=24, 48 etc., placed in nodes of usual crystalline lattices. In first time the E-phase, BN-analogs of “cubic graphite” and carbyn were synthesized in supercritical fluid gazostat at T<1000°C, P<200MPa. Their structures were interpretated as being the hyperdiamond fullerite HDF-$B_{12}N_{12}$, simple cubic fullerite SCF-$B_{12}N_{12}$, and nanotubular crystals respectively. Calculated parameters of unit cells and densities was shown to be in good agreement with X-ray diffraction patterns. Equation of states, energy band structure, electronic density of states, and bulk modula of three boron nitride fulborenite crystals HDF-$B_{12}N_{12}$, SCF-$B_{12}N_{12}$, SCF-$B_{24}N_{24}$ were calculated for the first time by FLAPW method. Remarkably that bulk module of HDF-$B_{12}N_{12}$ (B=590 GPa) was calculated to be greater then for diamond.

NEXAFS spectra of polymer-nanocarbon composites

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Numerous polymer-nanocarbon composites applications (e.g. electroluminescence, tribology, optical limiting, geology, thermal ignition) are being continuously documented. This provides firm impetus for the studies of the structure and properties of such composites. Though the studies of electronic subsystem of polymer-nanocarbon composites are known, the near edge X-ray absorption fine structure (NEXAFS) spectra of these composites have not yet been analyzed. We are addressing this problem through comparison the NEXAFS spectra of several polymer-nanocarbon composites. NEXAFS spectra of neat fullerene C_{60}, polystyrene (PS)-C_{60}, polymethylmethacrylate (PMMA)-C_{60} and PMMA-multiwall nanotubes composites were measured. The differences in the shape and intensity of LUMO (284.7 eV), LUMO+1 (286.1 eV), LUMO+3 (288.4) bands of neat C_{60} compared to fullerene imbedded into PMMA matrix are observed. Sensitivity of NEXAFS spectra to the intensity of fullerene LUMO bands for PS-C_{60} composite subjected to various heat treatements is additionally evidenced. We discuss the models explaining these effects in relation to vibrational subsystem of the polymer in presence of nanocarbon fillers.

Structural formation peculiarities of the carbon deposits originated from the accelerated C_{60} atoms

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It is known [1-4] that the structure of the films formed by depositing the accelerated molecules of C_{60} depends on the energy of the falling particles and the substrate temperature. The hard carbon structures up to nanocrystaline diamond are formed when the energy of ions in the incident beam exceeds of 1 keV and the substrate is kept approximately at room temperature [2]. Increasing the substrate temperature over the 500K at the ion energy of 5 keV stimulates the formation of the non-transparent well conducting films (~100 Ohm/?) of graphite structure.

In this work it has been shown that decreasing the energy of the incident C_{60} molecules down to 1-2 keV under higher surface temperature causes to grow hard transparent high resistive films. For example, the threshold of the graphitization rises to 700-800K at the ion energy of 2 keV. The dependence of the ion energy of C_{60} from 1 to 5 keV on the structural properties of the films was investigated. The nanoindentation technique was applied to study mechanical properties of the films.

The peculiarities of the structure formation of the carbon deposits at the ion energy over 1 keV were described in the frame of the hydrodynamic model of the shock waves that appear under shocks of accelerated atoms onto growing surface. It was shown the conformity between characteristics of the arising shock waves and structural peculiarities of the carbon deposits.

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Modification of iron nanoclusters by perfluorinated radicals

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Iron nanoclusters modified by perfluorinated radicals were obtained. Self-assembly of this particles was carried out by gas-core copyrolysis of pentacarbonyl iron with perfluorinated dialkylpolysulphides.

Due to formation of strong bound Fe-S-C, considered particles are stable in a broad spectrum of temperature. Perfluorinated radicals protect iron nanocluster from influence of different aggressive conditions.

Initial polysulphides were obtained in the following ways:

$$CF_3OCF_2CF_2CF_2OCF{=}CF_2 \xrightarrow{IF_5,\ I_2} CF_3OCF_2CF_2CF_2OCF_2CF_2I \xrightarrow{S} \text{S-13O2}$$

$$CF_3I \xrightarrow{S} \text{S-3}$$

It is possible to obtain nanoparticles of controlled size varying temperature of copyrolysis and structure of perfluorinated radical.

Unexpected magnetic characteristics were determined. Nanoparticles, obtained from different conditions, possess different magnetic characteristics. Dependence of particles’ size on conditions of synthesis was studied. These stable nanoclasters can be homogenized in broad variety of solvents. Thus, these properties allows using it in different fields of application. It could be quite attractive to create liquid and solid composite materials possessing magnetic properties.

Regular arrays of nanowires from asbestos nanotube-templated nanocrystals

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Nanowires are considered as the most prospective elements in future electronic and photonic devices. Among many nanofabrication approaches, templating nanowires in nanotubes offers versatility through the choice of nanotube and “guest” materials, tuneability of wire diameter and array topology and mechanical stability.

We present a simple approach to nanowire formation from pre-formed CdTe nanocrystals (NCs), optical properties of which are the function of NC size. NCs were embedded in channels of chrysotile asbestos (CA) nanotubes. Owing to macroscopic size of CA nanotubes, their perfect alignment and optical transparency, the unique bulk array of nanowires was prepared.

First, nanotubes were infiltrated by soaking NCs from a suspension under capillary forces. As revealed by TEM inspection, such samples are very lightly loaded with NCs. Since nanowires in CA are all parallel and well separated in space, measured spectra refer to a single nanowire. The optical transmission and photoluminescence (PL) of NC-CA composites remain isotropied that reflects the absence of NC-NC interaction. Alternatively, interaction of NCs with oxygen defects at the nanotube surface was observed. In low loaded NC-CA pumping of defect luminescence through trapping excitations from NCs was revealed.

Impregnation of nanotubes in the pressurised cell leads to denser NC impregnation. PL of heavy-loaded CA shows anisotropy with respect to the tube axis, pointing to NC-NC interaction along the tube and, thus, a nanowire formation. The parameter of the optical anisotropy changes with temperature, indicating, provisionally, the degree of NC mobility in the channel. Excitation trapping by defects is negligible at this level of impregnation.

This method is not limited to CdTe NCs, similar approach was applied, e.g., to Au nanoparticles in pursue for optical metamaterials.

Dipole moment of fullerene and basic structural unit of shungite carbon

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Structural units of shungite carbon (ShC) in the form of “bowls” characterizing by nonplanar structure with dimensions of less than 1 nm are easily transformed into aqueous dispersions. Their mobility explains metastability of ShC and a wide range of its physical chemical properties. Elementary particles in powdered fullerenes and fullerene soot (FS) are 0.45 and 0.6 nm in size, respectively [1]. The structure of soot nanoclusters is not in equilibrium and is changed substantially by various solvents. In addition to fullerenes and carbon particles (ions and atoms), FS contains fullerene fragments. We assume that these curved graphene stacks “bowls” in ShC and fullerene fragments in the case of FS have to possess dipole moment and provide polarity sufficient for complexation with water.

Dipole moments of fullerene C_{60}, FS and ShC structural units that precipitated from water were determined in diluted solutions at 293K using the method, described in [2]. It was established that the dipole moment value of C_{60} is correlated with its solubility parameters in different solvents. The dipole moment values determined under infinite dilution conditions are as follows: 1.38 D, 1.1 D and 0.84 D in benzene (1), toluene (2) and ortho-xylene (3), respectively.

Considering that solvent 3 is the thermodynamically best solvent for C_{60}, one may assume that the dipole moment value 0.84 D corresponds to the dipole moment of isolated C_{60} molecule ($?_0$). A rise in the dipole moment values in solvents 1 and 2 shows that C_{60} molecules are associated with Kirkwood correlation parameter g=2-3, $g = ?^2/(?_0)^2$. Dipole moment values for shungite carbon “bowls” in diluted toluene solutions is $? = 6.5$ D. Thus it follows from the study of the dipole moments of the nanocarbon units that unlike weakly polar C_{60}, the “bowl” has a high polarity.

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Electronic energy structure of gold nanoclusters on oxidized surface Ni(755)

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Recently nanoclusters of noble metals supported on a various oxide surfaces attract enhanced interest since they can exhibit high catalytic activity, particularly in oxidation of CO. Several theories have been suggested to describe this effect. One of them emphasizes the role of noble atoms in ionic state in the catalytic reaction. The presence of these noble atoms in ionic state determines the catalytic activity of the system. In several experiments the ionic state of gold atoms has been achieved on defect-rich surfaces with O-vacancies or with steps.

The aim of this work was to prepare oxidized stepped surface Ni(755) and to investigate the electronic energy structure of gold clusters formed of adsorbed gold atoms on this surface. It has been shown that oxidization of stepped Ni(755) surface is followed by formation of well-ordered uniform structure similar to O(2×2) that formed on flat Ni(111). On the fig. 1(a) the (2×2) superstructure of oxygen atoms is observed within the limits of terrace. According to PES and STM investigations the size of the formed clusters on such stepped surfaces is limited by the terrace width that leads to their uniform size distribution.

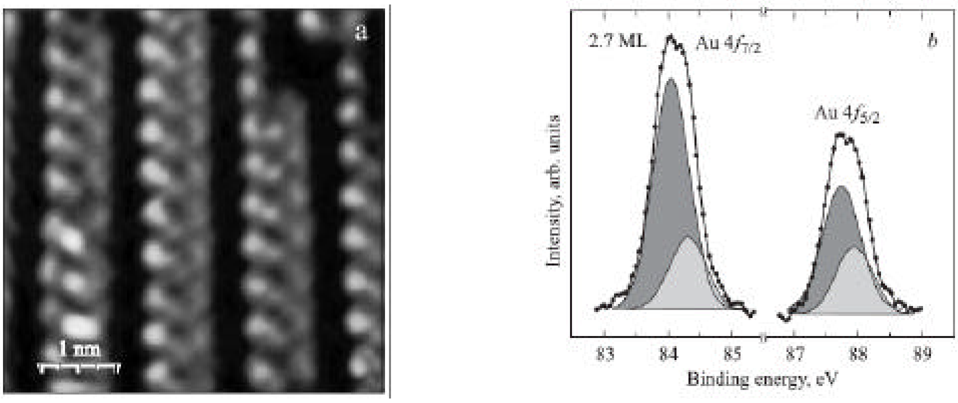

Figure1. (a) STM image of oxidized Ni(755); (b) Au $4f_{5/2,7/2}$ core level spectra from 2.7 ML of gold on oxidized Ni(755). The fitting procedure gives two spectral components. The area under curve of partially oxidized gold atoms is painted over by light grey color.

Au 4f5/2,7/2 core level spectrum from 2.7 ML of gold on oxidized Ni(755) is shown on fig. 1(b). The spectral components with binding energies 84.0±0.1 eV and 87.7±0.1 eV are characteristic for bulk metallic state of gold. Two additional spectral components appear with energies 84.3±0.1 eV and 87.9±0.1 eV. It is assumed that it is connected with partial oxidation of gold atoms with participation of surface defects inhered in stepped relief of nickel substrate.

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Influence of a structural condition of carbon on thermoelectric properties Bi_2Te_3

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For research of influence of a structural condition of carbon on experimental values thermopower telluride of bismuth at production of samples we have decided to take advantage of a method of powder metallurgy as other methods of introduction of carbon in matrix Bi_2Te_3 do not allow to achieve isotropic distribution filler on volume of a matrix.

Interest to similar matrix structures is caused by that such conditions of carbon as nanotubes and nanofibers in the form of floccus [1,2] and low compacting macroscopical structures [3] have high enough values thermopower and conductivity.

Samples were made in the form of briquettes in the size 10?10?5 mm^3. Thermopower it was measured by a method presented in work [4].

In work has been made comparison differential thermopower (S), conductivity (s) and thermoelectric good quality (ZT) depending on a volume fraction of carbon for various structural conditions.

It is shown, that introduction in matrix Bi_2Te_3 20 vol.% of a powder compacting MWNTs with bulk density 0.4 g/cm^3 result to growth thermopower from + 70 ?V/K up to + 90 ?V/K and to increase in conductivity at 60%.

At use as filler a powder individual MWNTs, the increase thermopower is observed from + 70 ?V/K up to + 95 ?V/K and growth of conductivity on 65%.

The estimation of change of size of thermoelectric good quality shows increase ZT at 35% in the first case and 50% in the second.

Use nano- and polycrystalline graphite, and also carbon CNF does not lead to similar improvements of thermoelectric good quality (ZT) an researched material, because of sharp increase in factor of heat conductivity.

Thus, by us it is experimentally shown, that use MWCNs as filler matrixes Bi_2Te_3 leads to significant improvement of thermoelectric properties, i.e. creating composit structure with inclusions nano-size conditions, it is possible to increase thermoelectric properties considerably.

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Activated by potassium ions flow field emitters with fullerene coating in strong electric fields

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Field emitters with protective fullerene coatings were worked out by this report authors. Such emitters are promising for electron devices operating under technical vacuum conditions. As fullerene coatings have high (more than 5 eV) work function value it causes the operating voltage increase. Earlier we found the possibility of work function decrease activating the fullerene coatings by the potassium ion flow. This activation reduced the operating voltage almost twice. Investigations of the activation process were performed at small electric fields and collected currents near 10 nA. But in practice, it is important to understand, if it is possible to use the fullerene coating treated by the ion flow at high electric fields and essentially more currents. This paper contains the first data regarding the influence of high electric fields on the emission characteristics of fullerene coatings activated by potassium ions. The coatings were formed on submicron tungsten tip with carbide tungsten layer on the surface. The coatings formation and activation were performed by the three-stage method [1] that was worked out in our laboratory. The fullerene molecule deposition and ion treatment of fullerene coatings were alternated. The influence of electric field on emission characteristic became noticeable only when collected current exceeded 2-3 μA. Results depended on the thickness of fullerene layers and the tip temperature during coating formation. The greatest current was collected from thick enough fullerene coating (5+2+2 monolayers), that was deposited on the tip heated to 500K. In this case, when the current exceeded 2-3 μA, it was observed the increase of its value at invariable voltage. At the same voltage, the current quickly (during an hour) became 10 times greater, and only then current changes were practically ceased. The coating was stable and was not destroyed at currents up to 50-60 μA. The structure and emission characteristics of the coating almost did not change after exposition at room temperature in residual gas atmosphere during more than twenty four hours. Thus, performed experiments showed the possibility to obtain large enough current from fullerene-coated field emitters activated by potassium ion flow. This work was supported by the Russian Foundation for Basic Research (grant 05-02-16936).

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Different conductive phases of C_{60} induced by high pressures up to 50 GPa

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The phase composition of Ñ$_{60}$ at given values of pressure P and temperature T depends on both the starting material (preliminary sintered at high pressures and high temperatures – HPHT treatment) and the way of reaching these P and T values (e.g., isobaric heating or isothermal compression). In this work the resistivity of pristine fullerite C_{60} was studied in the course of change of both pressures up to 50 GPa and temperature from 77 to 450K.

High pressures have been generated in the high pressure cell with synthetic carbonado-type diamond anvils. The anvils are good conductors and can be used as electric contacts. The method used allows us to study the same sample at successive increasing and decreasing pressure.

Resistivity peculiarities were identified with the known phase transitions of fullerite. The scheme of consequent phase transformation under high pressures and/or temperatures is suggested to be as follows: the molecular crystal C_{60} (fcc structure) ⇒ polymerized 2D and 3D conductive phases ⇒ a mixture of polymerized and amorphous phases ⇒ an amorphous phase. The resistivity relaxation kinetics at changing pressure was studied. Phase transitions of fullerite C_{60} appeared consequently in the course of HPHT treatment are accompanied by changes in resistance, which can be of quite different magnitude (from hundreds Ohm to hundreds MOhm) and different dependence on temperature.

Critical pressures for the transitions depended on conditions and duration of preliminary HPHT treatment. This fact, as well as smeared character of the transitions are connected with long relaxation time, which turned out to be of ~140 min. The different phase compositions of fullerite obtained after preliminary HPHT treatment may be a result of the existence of the long relaxation times.

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Carbon nanostructure formation via catalytic pyrolysis of benzene

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The aim of this work was to ascertain the correlations between the features of different carbon nanostructures observed and their specific preparation conditions via benzene pyrolysis.

Several series of syntheses were carried out with either iron pentacarbonyle or ferrocene as precatalyst. In each series we controlled the influence of the various parameters (such as process temperature, gas flow velocity, benzene flow rate, catalyst concentration, and composition of the vapour-gas mixture) on the yield and morphological peculiarities of the obtained products. In syntheses with ferrocene, the reactor pressure was also varied from atmospheric to a reduced one (~0.8 atm). A comprehensive study of synthesized deposits was accomplished by SEM, TEM, HRTEM, X-Ray, and Raman methods. Details of the analyses, observed features and formation mechanisms of the different carbon nanostructures will be presented.

One-dimensional chains of C_{60} molecules on Ni(755)

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Since the discovery of fullerenes in 1985 a huge amount of studies focused on their physical and chemical properties were performed. Because many intriguing properties of C_{60} emerge when these molecules are deposited onto solid surfaces, the ordering of C_{60} and its interaction to substrate were concerned in a number of works.

An important issue is the synthesis of low-dimensional molecular nanostructures resulted from the self-organization of C_{60} on single-crystal surfaces. Depending on the coverage and the structure of substrate, C_{60} can be found in different geometrical arrangements varying from small clusters to well-ordered molecular films. If the surface used as a substrate is geometrically anisotropic it can be expected that deposited fullerenes will form a low-dimensional structures. In this work we have investigated the possibility to create periodic one-dimensional chains of fullerenes supported on metallic surfaces.

The common idea often exploited for synthesis of nanostructures is the effect of step-decoration upon deposition onto the stepped single-crystal surfaces. In order to create separate chains of C_{60} the width of the steps should appropriately exceed the diameter of fullerene molecule. We have found that vicinal surface Ni(755) is suitable for this purpose. At room temperature the steps on this template are well-ordered and separated by nearly 25 A. We have investigated self-assembly of submonolayer amounts of C_{60} deposited onto Ni(755) by means of scanning tunneling microscopy.

It was found that deposition of C_{60} even at room temperature results in self-organization of molecular chains aligned preferably to the step edges of Ni substrate. It was also shown that neither increase of the coverage up to 0.5 monolayer nor moderate annealing can change this behavior.

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Geometrical flexibility of a graphite monolayer

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As is well known, there is a variety of carbon nanostructures with atomic structure that exhibit a considerable degree of similarity to the structure of graphite. On the one hand, quasi-two-dimensionality of the graphite crystal structure gives the possibility for existence of graphene, i.e. graphite monolayer. On the other hand, there are such structures as fullerenes, carbon nanotubes, etc. which atomic structure fairly resembles “curved” graphene. The question that arises here is: what are the relations between graphene and the other carbon structures, or whether can graphite monolayer be “curved” and what properties will it have? In order to answer this question in this work we investigated graphene synthesized on different geometrically nonuniform surfaces that have boundaries between two surfaces with different crystallographic orientations.

Graphite monolayer is well investigated on some flat surfaces of single-crystals, for example on Ni(111) where it forms good epitaxial film. In this work the next surfaces were chosen to be the substrates for graphene synthesis:

- stepped surface Ni(755) with (111) orientation of the step terrace. This surface will contain boundaries between epitaxial and nonepitaxial areas;
- stepped Ni(771) with (110) orientation of the step terrace which has no epitaxial surface areas;
- flat Ni(110) with surface lattice unit cell incommensurate to graphite lattice;

The graphene coating synthesized on these surfaces was investigated by means of scanning tunnelling microscopy (STM). The results show that both stepped surfaces undergo faceting during graphene formation. At the same time graphene at the facet edges keeps its continuity, curves and covers faceted surface like a “carpet”. This conclusion exhibit a good agreement with the results of our theoretical calculation for graphene on Ni(110). This calculation shows that in the case of Ni(110) graphite monolayer is corrugated with the period determined by the substrate crystal structure. STM measurements performed for this system are in a good agreement with the results of the calculation.

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Spectro-microscopic observation of intercalated fullerenes

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Graphite has the structure of a layered crystal with a honeycomb-like arrangement of atoms within crystal planes. This material possesses a number of unique properties such as intercalation-induced superconductivity and an unusual quantum Hall effect. Most recently, the electronic structure of a single sheet of graphite (graphene) has attracted huge attention due to low-energy electron excitations resembling massless Dirac fermions [1] which were evidenced in several experimental transport studies. [2]

In relation to these findings, the fabrication of high-quality self-organized graphene sheets has become an important issue. A well-known technique of such fabrication is cracking of hydrocarbons on hot surfaces of transition metals (e.g., Ni) or their carbides. [3] It is further possible to convert graphene layers obtained in this way into quasi-freestanding graphene by passivating the interface to the substrate in order to block chemical interactions. This can be done by intercalation of chemically neutral third element like noble metals [4] or, ideally, highly symmetric molecules similar to graphene.

In our work we test whether it is principally possibile to fabricate nearly free graphene sheets supported on fullerenes. Intercalation of C_{60} under graphene prepared by cracking of propylene on Ni(111) was evidenced spectro-microscopically by means of scanning tunneling microscopy (STM). Molecules are seen through the graphene carpet as a result of a unique bias-dependent spectroscopic contrast which is induced into the graphene by lifting the chemical interaction to Ni. The credibility of our results is supported by simple model calculations of local differential conductivity at the sites of trapped fullerenes and between them.

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Evaluation of physical-chemical parameters peculiar to the sorption in bulk of polymer nanocomposites

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Method of reversed phase gas chromatography (RPGC) is presently considered as the most informative one at the study on the process of low-molecular matters distribution in polymer matrix. Problems arise however when the method employed for sorption physical-chemical characterization in micro-heterogenous polymer systems (e.g. polyblock systems, nanocomposites), as there are several mechanisms of sorbate molecules distribution in polymer matrix. The determination of physical-chemical parameters of low-molecular substances sorption in micro- heterogenous systems uses RPGC method.

A sorption model has been suggested that is based on the processes of competitive solvation of both polymer matrix macrochains and low molecules at the interface of the micro- heterogenous systems. An analyses of mathematical expression which is based on suggested model made it possible to obtain expression for the evaluation of retention volumes in marginal cases of infinitesimal and infinite quantities of sample. The equation of retention volume for infinite samples has been used in the calculation of dissolution partial component that is of great importance in practice. It also enters formulae of sorption thermodynamic parameters. Temperature effect on dissolution component (retention diagram) has been determined. The diagram has been analyzed and expressions derived to calculate excess partial molar volumes within wide range of sorbates. Analysis of the data file obtained is quite useful in the investigation of fine supramolecular structures of polymer systems. The simulation patterns obtained and so mathematical analysis have been used for the evaluation of thermodynamic parameters of nanocarbons particle.

At the first step of our work we experimentally define the surface energy of high-dispersion oxide silicon. These experimental results obtained by attached method are in agreement with literary data and so this method was applied to investigations of other nanodispersion materials. The calculations show one can place nanocarbons particles in the following order *fullerenes-nanodiamonds- nanotubes* in accordance with the value of their surface activity.

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The third, molecular, form of carbon - fullerenes, fullerites and fullerides. Pre-hystory, discovery and physical properties

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A brief review is being done on the pre-history [1 – 3] and discovery [4] of fullerenes that make the third, molecular, form of carbon. Higher and smaller fullerenes. A family of fulerenes. The elaboration of methods for the production, separation and deep purification of fullerenes in quantities enough for growing crystals of macroscopic sizes [5]. Fullerites and fullerides. Superconductivity of fullerides. Intermolecular forces in fullerites. The Girifalco potential is presented for eight orientationally disordered phases of fullerites from C_{28} to C_{96} and its generalization is made for the interactions between the different fullerene molecules, C_m and C_n.

The thermodynamic properties of the high-temperature modifications of a family of the fullerites, from C_{36} up to the C_{96}, calculated [6] in equilibrium with their saturated vapors on the basis of the correlative method of the unsymmetrized self-consistent field that enables one to take into account the strong anharmonicity of the lattice vibrations, are discussed. The calculations were accomplished up to the temperature of loss of stability (spinodal point) T_s. The behavior of some characteristics is considered in their dependence on the number of atoms in the molecule.

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Fractal aggregation of carbon nanotubes in liquid mediums and their application in nanocomposite materials

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In solutions of toluene and acetone, carbon nanotubes deposit on the bottom of the vessel and create percolate fractal aggregates ranging in size from 5 to 15 μm. In distilled water, the size of the fractal aggregates is 30 μm. For their effective usage in nanocomposite materials, carbon nanotubes need to be dispersed throughout the liquid medium. Due to the small size of the fractal aggregates (5-30 μm), the carbon nanotubes in this study are ideally suited. Different building materials were nanomodified by the introduction of carbon nanotubes. Morphology and internal structure of nanomodified materials were studied by scanning electron microscopy. The hardness of building glass containing 1% carbon nanotubes was 5 times greater when compared to non-nanomodified glass. Nanomodified building glass has spherical pores ranging in size from nanometers to micrometers. Hardness of concrete nanomodified with 1-2% carbon nanotubes is more than 2.5 times greater in comparison with non-nanomodified concrete since concrete containing carbon nanotubes has fewer pores.

Arc synthesis and mechanism of ZnO-nanostructure formation

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ZnO-nanostructures have been the subject of intense research within some last years. To widen the range of ZnO - nanostructures and the methods used, the arc method has been tested [1]. The discharge electrodes were Zn- rods 3.5 mm in diameter; the working gas was O_2. The discharge chamber 40 mm in diameter and high was 100 mm. The arc discharge regime: current –80 A, tention-25 V.

On the basis of an analysis of the morphology of synthesis products, the mechanism of their formation is proposed. On the passage of current, the heated Zn material propagates from the contact area in the form of Zn - claster vapor. On the motion of Zn-clasters in the O_2 - atmosphere, the reaction $Zn + O_2 > ZnO_x$ takes place. The product that reaches the wall condenses and transforms from sheets to rolls and then to structures at the ends in the form of needles. On the free space, a part of the material crystallizes as bineedles, trineedles and tetraneedles. Nanostructures have different time of formation. The product condenses on the chamber wall as white snow.

The absence of catalyst and intermediate liquid phase speaks for the vapor-solid growth mechanism.

Characteristic dimensions of structures: length ~ 1µm, diameter: hundreds of nanometers.

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Space- and time-current spectroscopy of polypyrrole nanowires in chrysotile asbestos matrix

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The arrays of polypyrrole nanowires we synthesized inside nanotubes of natural chrysotile asbestos mineral. This mineral consist of parallel identical nanotubes that a very regularly packed. Inner diameters of nanotubes varied from 2 nm to 20 nm depending on the origin of asbestos mineral, and the intertube distance is about 30 nm. The length of such nanonanotubes may be up to 1 cm and the total number of nanotubes is 10^7–10^{10} per sample. Embedding of some substances into nanotubes of asbestos leads to formation of identical parallel isolated nanowires. In our case we filled the arrays of nanotubes with pyrrole from gase phase and realized the polymerization process inside these nanotubes [1].

The study of a new class of the semi-insulating materials, namely, asbestoses filled with nanoscaled components using the non-steady-state photoelectromotive force (photo-EMF) technique is the main goal of this paper. The non-steady-state photo-EMF technique based on the detection of the alternating electric current arising in the sample illuminated by an oscillating interference pattern is the most versatile and advanced method. The photo-EMF technique allows determination of the number of photoelectric parameters (conductivity, carrier sign, lifetime, diffusion length, and drift mobility), and can be applied for the investigation of both non-centrosymmetric and centrosymmetric media.

The presence of the effect of the non-steady-state photo-EMF in new class of materials -- polypyrrole nanowires is the first result that should be pointed out. In spite of the small signal amplitudes we can obtain reliable results by the use of high sensitive lock-in nanovoltmeter with the integration time up to 100 s and by the use of the additional signal accumulation and processing in the computer. The diffusion length of photocarriers was found to be L_D=0.18 μm.

To summarize, we have investigated the effect of the non-steady-state photo-EMF in polypyrrole nanowires within chrysotile asbestos matrix. The detected signal revealed the behavior similar to the one typical for widegap semiconductor crystals. The conductivity of the material and diffusion length of photocarriers were estimated. The observed time dependence of the detected signal is explained in terms of transition between conductive and insulating states of polypyrrole. As polymers and their nanostructures often demonstrate ionic conductivity the further investigations of such materials may reveal the necessity to rebuild the theory of the non-steady-state photo-EMF effect.

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Synthesis of water-soluble fullerene derivatives for medicinal applications

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Water soluble fullerene derivatives exhibited a number of exiting biological activities and have a potential to be applied as pharmaceuticals. Therefore, this field attracts attention of many researchers worldwide [1]. Progressive development of medicinal chemistry of fullerenes is limited now mostly by poor availability of highly soluble in water fullerene compounds with well-defined composition and structure.

In this presentation we summarize our results on the development of methods for large-scale preparation of water soluble fullerene compounds.

1. Amine derivatives of [60]fullerene were prepared in a photochemical reaction of C_{60} with piperazines. The tetraaminofullerenes were converted for the first time to salts that exhibited pronounced solubility in water (i.e. 200-300 mg/ml) [2].
2. Highly water-soluble aminated derivatives of C_{60} were prepared starting from halofullerenes $C_{60}Cl_6$, $C_{60}Cl_{30}$, $C_{60}Cl_{24}$ and $C_{60}F_{36}$ [3].
3. Friedel-Crafts arylation of $C_{60}Cl_6$ was used for efficient preparation of novel polycarboxylic fullerene derivatives. Solubility of the prepared acids in water in the form of salts with alkali metal cations reaches 150-200 mg/ml [4].

Antiviral and cytotoxity studies were carried out on the synthesized compounds. The carboxylic acid derivatives of C_{60} showed appreciable activity against HIV in combination with low toxicity. Some amine derivatives of C_{60} can be considered as inhibitors of Reovirus-1 and Sindbis virus; these fullerene compounds clearly outperform ribavirin in the tests.

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The experimental studies on the optimization of carbon nanotubes manufacture methods, methods of nanotubes introduction into matrix and methods of matrix modification

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Polymeric composite materials surely occupy there niche in aeronautical engineering as they show remarkable specific values of static strength and stiffness, vibration resistance, cyclic load endurance, dimensional stability over a wide range of temperatures. For the technological approaches aimed at the increase of epoxy matrix plastic deformation level, adhesion strength at the reinforcing fiber/polymeric matrix interface use the modification of epoxy matrix with carbon nanotubes.

We offer nanotubes 8 nm in diameter which possess a wide variety of advantages:

They easily dissolve in acetone which is very important as we use alcohol-acetone solutions of epoxy resins;

They are easily introduced into epoxy matrix.

In the course of our R&D work we considered the peculiarities of epoxy matrix molecular composition and supermolecular structure formation. It has been found that carbon nanotubes have a profound effect on the epoxy resin rheology, gel phase deformability, morphology, elastic deformation of the vitrified polymer.

A series of experiments on the determination of CFRP (carbon fiber reinforced plastic) ultimate tensile and compression strength and modulus of elasticity in tension has been performed. It is shown that the stress-strain properties of the nanomodified CFRP are 10-25% higher than those of the standard CFRP. The most significant results in this case have been obtained for the specimens made of CFRP with the reinforcement pattern simulating the real skins of the “PROTON-M” nose fairings and on the determination of the ultimate compression strength in zero direction. The results obtained support our expectations concerning the strengthening of epoxy matrix with nanotubes and agree well with the data published on this problem.

Nanosized carbon hills on Pt(111). Formation and properties

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Formation of carbon nanoobjects such as fullerenes, nanotubes, onions, nanocones etc. is very challenging and promising sphere of carbon chemistry. The initial steps of the process are crucial for the morphology and properties of the materials. The components for the nanoparticles formation as well as the condition under which this formation occur (temperature, buffer gases etc.) play an important role. This process is very difficult to investigate because of very short passing time and huge variety of simultaneous stages. We try to simulate on the platinum monocrystal all the process of the catalytic growth i.e. decomposition of the hydrocarbons, dissolution of carbon atoms, their segregation to the surface and finale construction of carbon objects.

Following this strategy the carbon cover is fed both carbon atoms originated from decomposition of hydrocarbons and those preliminary having been absorbed by the platinum bulk. Such a way on the surface we have isolated carbon atoms as well as carbon fragments from the hydrocarbons as elements to form the carbon structures. There is possibility to change concentration and types of the elements by varying temperature, saturation time, type of hydrocarbon etc.

Depending on the growth conditions, the spectroscopic features of the films change essentially. The most interesting one is “high energetic covers” - HEC (we refer it to the films, obtained from ethylene, which C1s lines have BE more than 284.6eV). The film is quite different in XPS and Auger electron spectroscopy from planar graphite films and very similar in the characteristics to nanotubes and fullerenes layers. It was in the contrast with “low energetic covers” - LEC (we refer it to the films obtained from ethylene which C1s line position is lower than 284.4 eV) with features are close to the ones of graphite.

Using STM and RAM it was found that HEC films consist of carbon hills with diameters about nanometer, ordered in the hexagonal symmetry. The properties of the films such as combustion and thermal stability have been investigated.

IR-Fourier spectral research of structural transformations in low dimensional glassy nanocarbon

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Last decade are actively investigated fullerenes and nanotubes carbon structures as actual semi-conductor and superconductor in micro- and nanoelectronics, and as actively filtering materials in chemistry and ecology. For creation of composite materials on the basis of nanocrystaline structures a prominent aspect is studying structure and phonon’s spectrum of initial and final materials.

Phonon’s structure is in detail enough investigated Raman spectra (RS) of amorphous and crystal carbons. However, not all vibration states in view of an alternative selection rule are active in Raman. Research of vibration states in IR-spectra of the condensed carbon is complicated by intensive not selective absorption of free carriers of a charge. The phonon spectrum in a series of nanocrystaline glassy carbon (GC) with monotonously changing degree perfection of crystal structure is investigated in this work. Thermal processing of samples in the inert environment in the field of temperatures 1300–3000^{o}C has allowed to change the sizes of fragments of coherent dispersion in a range 2.5–5.4 nm. The natural surface of samples was investigated at a corner of reflection 20^{o} on IFS-88 (Bruker) spectrometer in wide spectral area: 5000-400 cm^{-1} with the sanction of 2 cm^{-1} and in a regime of accumulation up to hundred scans.

According to modern representations, atoms of carbon in structural motives of transitive forms of carbon are in various valent hybrid states: sp^{n}- ($1 \le n \le 3$). And a number of researchers assumes, that nanocrystaline areas of coherent dispersion have structure multilayered fullerenes clusters [1]. Proceeding from the theoretical-group analysis of fragments of crystal structure in an IR-spectrum GC optical activity intraplane asymmetric vibrations of graphite’s atoms (D_{6h}^{4}) or fullerenes (I_h) frame mesh structures [1] should possess. Where concerning central point Ã of Brillouin zone following vibration states are active:

$$D_{6h}^{4} : \tilde{A}_{vibr} = A_{2u} + E_{1u} + 2E_{2g} ,$$

$$I_h : \tilde{A}_{vibr} = 2A_{2g} + 3T_{1g} + 4T_{2g} + 6G_g + 8H_g + A_u + 4T_{1u} + 5T_{2u} + 6G_u + 7H_u .$$

In experimental IR-Fourier spectra of GC are registered selective absorption bands of vibration states E_{1u} and T_{1u} in the field of 1600-1300 cm^{-1}, in 900-800 cm^{-1} (A_{2u}). Intensity and position of bands naturally change with growth of temperature of samples processing and correlates with results on research of Raman and ATR spectra on the given objects [2].

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The diffuse reflection spectroscopy of vibration states in nanocarbon clusters

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Optical properties of micro-, nanocrystal and amorphous materials on the basis of the condensed carbon are in detail enough investigated by Raman spectroscopy, IR- and UV-absorption of thin cuts and foils [1].

The most part of works is devoted to studying of spectral area from above 0.5 eV, results are interpreted on the basis of electronic transitions near the Fermi's level within the limits of electronic zone models of two- and three -dimensional graphite. The IR-optical area 0.5–0.01 eV in which vibration states of carbon should be active, is less studied [2].

In the given work on the basis of adapted to absorption media of a method of diffuse reflections spectroscopy (DRS) and an original device to the infrared (IR) spectrometer of quantitative studying of vibration states in nanocrystal carbon, on an example of pyrolitic carbon (PC) and glassy carbon (GC) is investigated. On the basis of the formula offered in work similar to Kubelka-Munk relation the influence of initial parameters of samples (concentration of substance, a degree of its depressiveness, frequency of radiation) on the factor of scattering are investigated.

In DRS -spectra of selective absorption in ranges of 1100-700 cm^{-1}, 1700-1200 cm^{-1}, 3400-1800 cm^{-1} are shown, that well enough correlates with features in a spectrum of function of density phonons states of condensed carbon with graphite's, fullerenes and carbon's chains motives. According to calculations of phonons states spectrum of graphite, at 850 cm^{-1} intraplane (A_{2u}) and 1580 cm^{-1} and interplane (E_{1u}) modes are active in the IR- absorption spectrum. In DRS -spectra of PC and GC are registered a wide bands of absorption on 900-800 cm^{-1} and maxima of absorption on 1510 and 1240 cm^{-1}, and also - features in the form of excesses in the field of 1570, 1350, 1020 cm^{-1} [3].

Interpretation of selective bans of absorption in DRS -spectra of nanocarbon materials is lead and correlate with Raman and IR-reflection spectra given samples [4].

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Elastic constants of nanocrystaline carbon

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Carbon in the condensed condition possesses the polymorphism connected with an opportunity of realization of various types of hybridization valent electronic states (sp-, sp^2-, sp^3-). Thus physical properties of materials on the basis of carbon change from typically metal up to dielectric. Pyrolitic carbon (PC) in the given classification belongs to hexagonal, polycrystalline structures consisting from graphite like of submicron particles, divided by less ordered carbon phase. PC possesses high chemical inertness, durability, heat- and electric current conductivity, the low porosity, increasing anisotropy of physical properties at increase in temperature of processing. All this defines high adaptability of PC to manufacture especially for creation of composite systems.

At calculations of mechanical, electronic and phonons properties of the condensed systems on the basis of carbon in the major parameter speed of distribution of ultrasonic waves and elastic constants of materials acts.

In work speed of distribution of ultrasonic waves (USW) in the region of frequencies of 0.5-25 MHz in PC- samples with monotonously changing structure is investigated. On the basis of the measured speeds longitudinal and transverse USW calculation of elastic constant PC- samples with temperatures of processing 2100-3200 ^{o}C is lead. Measurements of speed of waves are lead by means of ultrasonic spectrometer Andescope AST-2000 by a direct method of measurement the time of passage of a signal on known base.

The basic results of calculations of Jung module in two mutually perpendicular directions in relation to a plane of sedimentation PC are lead on the measured values of speeds longitudinal and transverse of USW. The error of measurement of speed makes 2-3%, for modules of elasticity - accordingly 5-7%.

Calculation of elastic constants was spent under formulas which included speeds of longitudinal and transverse waves (v_l, v_t), density (r) and factor Poisson (m=0.10-0.22) [1].

The results received in work under the order of size correspond to not numerous available data on measurements elastic constant nanocrystaline artificial graphite[2, 3].

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C_{60} and C_{70} compared by IR spectroscopy studies

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Fullerenes represent a very interesting class of compounds for their applications in science of materials [1-5]. C_{60} was synthesized by PNPI lab and C_{70} was received from Aldrich. C_{60} and C_{70} were studied utilizing IR spectroscopy method [6] to better understand slight structural differences; results will be discussed [7].

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Magnetic g-factor and specific electrical resistances of conducting materials of Ion-radical salts composted by different heterocyclic N-oxides with 7,7,8,8-tetracyanoquinodimetane

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Specific resistances of new heterocyclic N-oxides with 7,7,8,8-tetracyanoquinodimetane were measured [1-3]. As result para-position of substituent groups on the pyridine cycle was slightly influenced the behaviour of structures and increased very little the values of specific resistance (?). In the case of the introducing of the alkyl substituents with carbon long chain at the Oxygen atom in cations of N-oxides with TCQM the resistance were decreased quite a lot. All ion-radical salts with TCQM were paramagnetic and it's shown by the intensive absorption shift in EPR-spectrum (value of g-factor is correspond to 2.0029±0.0002) [4, 5]. These N-oxides were investigated in detail by DSC and IR spectroscopy.

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Microwave properties of composite with cobalt nanoclusters on aramide tissues

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Nanostructured materials containing ferromagnetic nanoclusters of 3d metals in an isolating amorphous matrix show various interesting microwave properties [1]. The effective absorption of electromagnetic waves at microwave frequencies allows us to consider the composites as perspective nanomaterials for thin broad-band absorbing covers [2].

We studied microwave properties of multilayer covers {a-C:H (Co) films on aramide tissues}, especially, reflection of the covers on Cu shield. Measurements were carried out by the irradiation method in 8-mm band using strongly emitting quarter-wave slit and horn detector [3]. In results the unexpected dependence of microwave reflection signal on the position of the screen (150×150 mm^2) in far region (>100λ) is observed.

A possible mechanism for observed behavior is considered on the basis of the concept of the dielectric and magnetic losses of nanocluster percolation network [4].

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Electrostatic Force Microscopy study of nanodiamonds on the silicon surface

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Nowadays different carbon nanostructures are used extensively in modern physics, medicine and biology. Because of their negative electron affinity nanodiamonds have a great potential as a high effective cold electron emitters.

In this work we use the dynamic electrostatic force microscopy (EFM) to study electrical properties of nanodiamond clusters on the silicone surface. Our samples were prepared by electrophoretical deposition of detonation nanodiamonds from organic solution on the highly doped silicon substrate. A special treatment of the solution with nanodiamonds was used to segregate the nanodiamond conglomerations [1]. A high temperature annealing was used to remove organic reagents from the sample surface.

EFM methodic allows obtaining the electrostatic force gradient distribution over the surface through the measurements of the phase shift of the cantilever oscillation. It was found that when the tip of the cantilever is positioned directly above the nanodiamond clusters the measurements of the phase contrast at different bias voltages between the sample and cantilever show that the value of the phase contrast linearly increases as the value of the bias voltage goes up. The positive sign of the phase contrast observed in the experiment corresponds to the attractive interaction between the cantilever and nanodiamond clusters. The type of interaction does not depend on polarity of the bias voltage. It is worth to note, that the electrostatic interaction between tip of the cantilever and clear silicon surface showed a minor effect on the phase contrast.

The appearance of the phase shift contrast could be due to the formation of the electrical contact between the shell of the nanodiamond clusters and the conductive substrate. Earlier the graphite shell on the nanodiamond clusters was found with the small angle X-ray scattering technique [2].

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Thermal conductivity and properties of urethane lacquer modified by nanocarbon materials

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We were studied the thermal conductivity of composites based on the two-component urethane lacquer with addition of well purified detonation nanodiamonds and natural micron size diamonds. The density of composites from natural 10-14 μm diamonds and nanodiamonds were also examined. The samples of a lacquer modified by copper were used as reference.

Both types of composites were prepared by modification of a lacquer at room temperature. It was revealed, that limiting concentration of copper in a lacquer and diamond and nanodiamonds in a lacquer makes ~70% on weight. For producing a cylindrical samples were located in fluoroplastic ditches with a diameter 5 mm and height ~20 mm and were densely closed.

The density measurements were realized by a hydrostatic weighing and the thermal conductivity of the samples was defined by a steady state heat flux technique. The dependences of density on concentration of copper and diamond are estimated in the assumption of density for copper (8.96 g/ccm), diamond (3.52 g/ccm) and the measured density of the hardened samples of a pure lacquer (1.3 g/ccm).

The density deviation from an estimated curves associates with a presence of air inclusions in samples. It was found that thermal conductivity rises with increase of modifying agent particles concentration in a lacquer.

Microdiamond and nanodiamond composites thermal conductivities were found to be about 5 W/(m*K).

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Investigation of process of drying of nanodiamonds

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In the presented work we have studied the acid properties of high-purified samples of detonation nanodiamond (DND).

The crystal qualities have been characterized by X-ray diffraction, scanning electron microscopy (SEM) and high resolution transmission microscopy (HRTEM). It has been shown that every DND particle consists of a diamond core of about 5 nm and a carbon-shell around the core. DND particles form a hierarchic structure with several levels of aggregation [1].

For these investigation we used the samples of DND with ash content less than 0.1% and content of magnetic impurities (Fe, Co etc) less than $1 \cdot 10^{-7}$ gramm-atom/gramm.

We have prepared the samples of clear DND from nanodiamond suspension by drying on air at different temperatures: 100, 130, 170, 200, 300, 350°C. Also we have prepared the restored 1% suspension of DND by sonicating (22 kHz, 60 J/g) in distilled water. For that the DND samples dried on air for 12 hrs were used.

Was shown that the acid properties of the restored DND suspension are not changed up to temperature of driying of 200°C. The region of stability of this suspension is the same with the region of stability of the initial (not dried) suspension. The own acidity of the restored suspension is same as that of the initial nanodiamond suspension (dissociation constant pK~ 4.3-4.5) [2]. But it is detected, that the behavior of the small angles X-ray scattering (SAXS) curves of these samples are different by analyzing the dependence of SAXS intensity I on wave vector q in region of q: $0.036<q<0.8$ A^{-1}. The slope of SAXS curves in logarithmic axes is the same for all samples dried at temperatures up to 200°C. This shows that the surface state of DNDs dried at temperatures up to 200°C does not change. On the other hand, some extra features in SAXS curves were observed. We suppose that these features may appear because of formation of extra scatters with sizes above 12–18 nm. This fact is the evidence that the sizes of aggregates of DNDs strongly change in the process of drying.

The acid properties of suspension prepared from samples dried at high temperatures (300-350°C) is changed. The region of stability of the restored suspension is broadened, the suspension is stable up to pH = 12 or more. The slope on SAXS curves in logarithmic axes are not the same and there are some extra features in the curves. Several possible explanations of the observed phenomena are presented.

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Cathodoluminescence studies of the nanodiamond particles

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We have recently reported about a new method for introducing metals into nanodiamond (ND). We have suggested that it cause by an exchange reaction of acids groups with hydrogen [1]. However we have not direct evidence of that fact till now. The use of cathodoluminescence (CL) method allows characterizing the valence state of different ions that are CL activators. In our case the rear earth ions introduction on the surface of ND may provide additional information about defects and impurities in ND particles.

The nanodiamond particles have been produced by detonation technique. The crystal qualities have been characterized by X-ray diffraction, SEM and HRTEM microscopy. The intercalation by rear earth metals been carried out by mixing metal salt solutions with a ND suspension. The CL emission of initial ND and the ones, intercalated by rear earth metals, have been investigated under room and low temperature. For the CL characterization electron-beam energy 10 keV is used.

Two broad components are dominant in the CL spectrum. The first is a very broad component with peak energy of 2.1 eV. The second is a green-blue component with asymmetric line shape (A-band). The main features of the last component are shoulder at 2.63 eV and broad peak extending to 3.5 eV. Comparison of the CL spectra with the spectra of known defects in natural and synthetic diamond, gave us possibility for identification the following luminescence centers: 2.1-eV band attributed to oxygen-containing center, and A-band attributed to defects at grain boundaries. The weak line 1.94 eV is associated with point defects concerned with nitrogen. The dependence of A-band upon the previous treatment of ND (annealed in hydrogen, intercalated by Uranyl ion) is discussed.

The CL in ND, activated by ions of $Eu^{3+}$and Sm^{3+} has been observed. The nature of the luminescence centers in ND intercalated by rear earth ions has been determined. The shape of the band concerned directly to the intercalation ions allows to make the conclusion about their presence at the surface of ND particles.

The equipments of a Center “Material study and diagnostics for advance technology” (Ioffe Institute, St.Petersburg, Russia) have been used at investigation of initial UNCD.

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Anomalous magnetoresistance of C_{60} and other organic semiconductors

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Transport in various thin-film organic semiconductors has been shown to have an anomalously high sensitivity to low magnetic fields at room temperature (RT). In particular, we report magnetoresistance (MR) for semiconducting oligomer and nonconjugated polymer materials in addition to small molecule and conjugated backbone polymer materials. For example, films of the light emitters poly(N-vinylcarbazole) and Alq_3 each have an MR response greater than 5% at an unusually low magnetic field of 100 Oe ($m_B H$ ~ 0.0006 meV) at an unusually high temperature of 300K ($k_B T$ ~ 26 meV). Increasing the spin-orbit coupling in Alq_3 films by doping with the phosphorescent sensitizers $Ir(ppy)_3$ or PtOEP strongly suppresses the MR signal. MR in thin films of the oligomer α-sexithiophene can be negative, similar to the behavior of other organic semiconductors, or positive depending on the temperature, layer thickness, or applied voltage. We have developed a model, termed Magnetoresistance by the Interconversion of Singlets and Triplets (MIST), accounting for this anomalous MR [1]. At zero field, the singlet and triplet e-h pair states are degenerate and the states can readily interconvert due to hyperfine interaction. Finite magnetic fields lift triplet degeneracy which affects the hyperfine interconversion of e-h pairs between singlet and triplet states. By changing the carrier recombination the MIST mechanism gives rise to a space-charge-limited current that depends on magnetic field, producing MR.

*In collaboration with J.D. Bergeson, D.M. Lincoln, and A.J. Epstein.

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Photoionization and vacancy decay of endohedral atoms

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It is demonstrated that the fullerene F (e.g.C_{60}) shell affects dramatically the photoionization of the endohedral atoms A@F leading to new resonances in the total and partial cross-sections, dipole and non-dipole angular anisotropy parameters, and photoelectrons spin polarization.

The calculations are performed within the framework of a very simple, so-called “orange skin”, model that makes it possible, in spite of its simplicity, to take into account the modification of atomic subshell due to its interaction with inner and outer atomic shells, as well as with the collectivized electrons of the fullerene. Main attention is concentrated on C_{60} as a fullerene.

In a fullerene the collectivization of about four electrons from each carbon atom (240 electrons in C_{60}) leads to the Giant resonance in its photoabsorption cross-section. It is demonstrated that the effect of fullerene shell upon A@F cross-section essentially depends upon not only the magnitude, but also the shape of the Giant resonance. It can vary from almost total screening of the inner atom A from incoming photon beam to essential enhancement of its photoionization cross-section.

The fullerene shell impressively affects the vacancy decay in A@F due to opening new decay channels that are closed in isolated atoms A, and due to virtual excitation of the Giant fullerene resonance.

To determine the fullerene shell dynamic influence upon A@F photoionization and vacancy decay simple formula are derived based on an assumption that the F radius is much bigger than the atomic one. These formulae include only the fullerene radius and its dipole polarizability. The latter is expressed via fullerenes total photoabsorption cross section with the help of the dispersion relation. Concrete results are presented for A@C_{60}, where the photoabsorption cross-section is well-know.

The results demonstrate strong influence of C_{60} upon A@C_{60} photoionization and vacancy decay.

Kinetics of 2D-3D transformations of carbon nanostructures

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In this work we consider the gas-phase formation of carbon nanostructures from graphite sheets under high-energy processing, such as arc discharge or laser evaporation [1]. In order to obtain kinetic characteristics of the folding of a single graphite sheet and to examine its mechanism we carried out molecular dynamics simulations of this process.

Although the energy barrier of the process is very high, our simulations showed that the folding of a graphite sheet proceeds in about 1 ns at 3500K. This is explained by the formation of numerous defects, which increase the system entropy and, hence, substantially reduce its free energy at high temperatures. Defects are mainly formed in surface reactions and the folding occurs when the density of defects at one of the corners reaches its critical value.

During the simulation, the main reactions of defects were detected and then their kinetic characteristics were evaluated. The simulation showed that the most important reactions of defect transformation proceed with the breaking of only one bond. Furthermore, the mechanism of defect penetration into the interior of the graphite sheet is most likely associated with the formation of small defects adjacent to a ten or more-membered ring.

Based on the elementary processes examined, we suggested a simple scheme for determining the equilibrium densities of defects at sheet edges. According to this scheme, the minimal temperature at which the folding of graphite sheets can be observed experimentally is 2500K.

After the folding process is completed the further relaxation of the imperfect structure formed proceeds via the Stone–Wales rearrangements [2] and the modified Stone–Wales rearrangements of defects [3]. Nevertheless, these reactions involve many steps rather than one. The addition of carbon atoms and dimers [4] to defects was shown not to be more favorable than their addition to hexagons and it should not be considered as a way of reducing the number of defects.

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