Proceedings

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Proceedings

Second International Workshop Nanocarbon Photonics and Optoelectronics

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Editors:
Yury Svirko
Dmitry Lyashenko

Finland
1 - 6 August 2010

NPO2010 Schedule-at-a-Glance

	Monday, Aug 2	Tuesday, Aug 3	Wednesday, Aug 4	Thursday, Aug 5	Friday, Aug 6
	E-m properties	Photonics	Nc properties	Synthesis	Electron emission
9:00-9:50	*R. Saito*	*A. Ferrari*	*R. Baughman*	*V. Kuznetsov*	*V. Konov*
9:50-10:40	*H. Kataura*	*E. Obraztsova*	*A. Balandin*	*P. Hakonen*	*R. Nemanich*
10:40-11:00	**Coffee Break**	**Coffee Break**	**Coffee Break**	**Coffee Break**	**Coffee Break**
11:00-11:50	*S. Maksimenko*	*G Lanzani*	*H. Lipsanen*	*Oral presentations*	*Oral presentations*
11:50-12:40	*E. Kauppinen*	*H. Kuzmani*	*A. Loiseau*		
12:40-14:30	**Lunch**	**Lunch**	**Lunch**	**Lunch**	**Lunch**
14:30-16:00	*Oral presentations*	*Oral presentations*	*Visit to the University and Science park*	*Oral presentations*	*R. Won*
16:00-16:20	**Coffee Break**	**Coffee Break**		**Coffee Break**	
16:20-17:40	*Oral presentations*	*Oral presentations*		*Oral presentations*	
18:00-19:30	**Welcome party**	**Dinner**	**Boat trip reception**	**Dinner**	**Farewell party**
19:30-21:00		*Poster session I*		*Poster Session II*	

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Welcome

The great diversity in the properties of nanostructured carbon allotropes such as fullerenes, carbon nanotubes, graphene and nanodiamonds has recently attracted a great deal of attention. The growing interest of research community to nanocarbons that was triggered by both fundamental problems and strong application potential of nanocarbon materials is major driving force behind the International Workshop Nanocarbon Photonics and Optoelectronics. The Workshop aims at an intensive and informal ideas exchange between researchers from around the globe and at providing opportunity for students and post-doctoral researchers to learn more about both fundamentals of nanocarbon materials and latest achievements in this rapidly developing field.

About 100 researchers and students from different countries had taken part in the first Workshop, which was held in the Holiday centre "Huhmari" in Eastern Finland in August 2008. The proceedings of the Workshop have been published in the special issue of Journal of Nanoelectronics and Optoelectronics (vol. 4, number 2, 2009). This year we are pleased to welcome you to the second Workshop "Nanocarbon Photonics and Optoelectronics".

We would like to welcome our plenary lecturers, researchers and students and thank them for taking part in the Workshop. We are grateful to our sponsors for their financial support, which has enabled us to offer moderate workshop fees and provide travel grants to our lecturers. We are also grateful to the University of Eastern Finland and other organizations that have helped in organizing the Workshop.

We hope that the workshop will be rewarding both scientifically and socially and that this week in Koli will give you an opportunity to enjoy the beauty of Scandinavian summer.

Yuri Svirko and Alexander Obraztsov

Workshop Chairs

Contents

Monday, August 2

Raman spectroscopy of graphene and single wall carbon nanotubes

Riichiro Saito

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Recent progress on Raman spectroscopy of graphene and single wall carbon nanotubes (SWNTs) is reviewed. First, optical transition energies E_{ii} of a SWNT exciton as a function of the chiral index (n,m) and the subband index i changes up to 100meV depending on the surrounding materials, which is known as an environmental effect. The environmental effect makes the (n,m) assignment difficult in the analysis of photoluminescence (PL) and resonance Raman spectra. Here, we propose an empirical function which scales the environmental effects on E_{ii} for a wide region of diameter and energy region. Using the correction terms, we can easily assign (n,m) with one parameter for each environmental material [1]. Next, we discuss Raman spectra as a function of the gate voltage applied to metallic SWNTs which show phonon softening phenomena (the Kohn Anomaly effect). Anisotropic electron-phonon interaction is relevant to chiral angle dependent Kohn anomaly effects [2-5]. Finally, we discuss the Raman spectra of graphene edges. In the case of a single-layer graphene, there are two types of edge structure, armchair and zigzag edges. In the zigzag edge, there are electronic edge states at the Fermi energy, while in the armchair edge, the D-band Raman spectra becomes strong. Such edge-shape dependent physical properties are useful for characterizing the edge structure by the Raman spectroscopy. We will report polarization dependence of Raman spectra at the edges, too [6].

This work is collaborated with Prof. J. S. Park, Mr. A. R. T. Nugraha, (TU), Dr. K. Sasaki (AIST), Prof. M. S. Dresselhaus group (MIT), Prof. A. Jorio and Prof. M. A. Pimenta's group (UFMG, Brazil) and is supported by KAKENHI (No. 20241023).

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HIGH YIELD METAL / SEMICONDUCTOR SEPARATION OF SINGLE-WALL CARBON NANOTUBES

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For the electronic, optical, and optoelectronic device applications of single-wall carbon nanotubes (SWCNTs), mixed production of metal and semiconductor phases was one of the most serious problems because they show completely different electronic and optical properties. It is known that density gradient ultracentrifugation (DGU) technique can separate metallic and semiconducting SWCNTs with high purity [1]. However, the separation process is so complicated and the scale up is difficult because of the limited rotor capacity. For the industrial application, more effective separation method was desired. Recently, we found a specific interaction between semiconducting SWCNT and agarose, and developed new separation methods using agarose gel [2-4]. These methods realized high purity separation with low cost, high speed, and high efficiency. In the latest separation method, we used only agarose gel beads and two surfactants, sodium dodecyl sulphate (SDS) for metallic SWCNTs and sodium deoxycholate (DOC) for semiconducting SWCNTs. Figure 1 shows the schematic pictures of the separation. The separation procedure is very simple and can be repeated for many times.
In this presentation, we will show the recent progress of our separation methods and some device applications, such as high-performance thin film transistors using semiconducting SWCNTs [5].

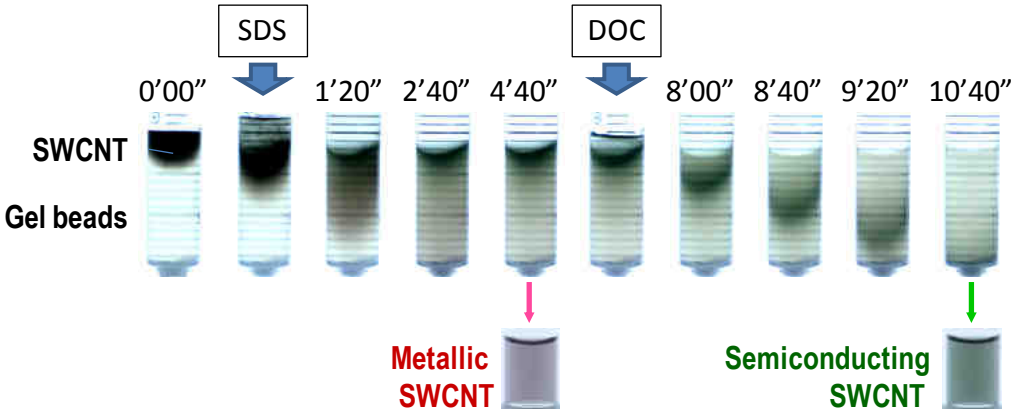

Figure 1. Pictures of continuous agarose gel beads separation of SWCNTs.

[1] M. S. Arnold *et al*, Nat. Nanotechnol. **1** (2006) 60.
[2] T. Tanaka *et al.*, Appl. Phys. Express **1** (2008) 114001.
[3] T. Tanaka *et al.*, Nano Lett. **9** (2009) 1497.
[4] T. Tanaka *et al.*, Appl. Phys. Express **2** (2009) 125002.
[5] S. Fujii *et al.*, Appl. Phys. Express **2** (2009) 071601.

Electromagnetic response of carbon nanotube-based composite materials

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The problem of design and fabrication of effective low-cost electromagnetic coatings for microwave frequencies became pressing nowadays, because of wide dissemination of their applications ranging from wireless network technologies, targeting radars, vehicle speed detection, electron spin resonance apparatus, etc. Light-weight nanocarbon-based additives became popular for producing effective EM polymer coatings. There are many possibilities to control EM properties of nanocarbon-based composites, and therefore to tailor their EM shielding capacities. Geometry and polarizability of individual filler constituents – the constitutive parameters of nanocarbon assemblies – as well as the permittivity of the host matrix and its affinity for carbon fillers can be pointed out as controllable factors. Among other nanocarbon fillers, carbon nanotubes (CNTs) attract especial attention due to their large aspect ratio, possibility to control orientation, and non-monotonous frequency dependence of scattering characteristics.

A rigorous theoretical investigation of electromagnetic scattering by an isolated CNT is a complicated task. In general, different physical factors contribute simultaneously into the effective constitutive parameters. Our theory is based on standard homogenization approaches that require the description of an isolated SWCNT as a point-polarizable object. In order to calculate the polarizability tensor of an isolated SWCNT, we combine the methods of classical electrodynamics and quantum kinetics. The latter means that the motion of π-electrons in an SWCNT is described as quantum motion of quasiparticles with a special dispersion law accounting for the hexagonal crystalline lattice and the quantization of transverse momentum. This allows us to formulate effective boundary conditions for the electromagnetic field on the surface of the SWCNT. Thus, the self-consistent problem of electromagnetic field together with π-electron dynamics is reduced to a boundary-value problem of classical electrodynamics. In order to calculate the plane-wave scattering amplitude of an isolated CNT taking into account finite-length effects, we applied the integral-equation technique to solve that boundary-value problem.

Our theory is applicable over wide temperature and frequency ranges (from microwave to ultraviolet), and encompasses composite materials comprising different types of single-walled and multi-walled CNTs. It yields a satisfactory explanation of available in literature experimental data for the absorption of CNT-based films in a wide frequency range. In particular, the theory explains a non-monotonous (non-Drude) frequency dependence of the conductivity of CNT composites in terahertz range.

The research was partially supported by the International Bureau BMBF (Germany) project BLR 08/001, the EU FP7 CACOMEL project FP7-247007, and the ISTC project B-1708.

SYNTHESIS AND DRY DEPOSITION OF CARBON NANOTUBES FOR FLEXIBLE TCE AND TFT APPLICATIONS

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We present mechanistic investigations on SWCNT formation mechanisms during floating catalyst synthesis from CO at ambient pressure and at temperature range 800-1100 ºC using iron nanoparticle catalyst. We discuss the effect of reactor operating temperature on the individual tube as well as bundle length and their diameter distributions, being determined both by electron microscopic as well as optical methods. Especially, we discuss the controll of tube chirality distributions via introducing trace amounts of CO_2 and NH_3 into the reactor.

Methods for SWCNT dry deposition at ambient temperature to manufacture transparent thin film field effect transistor (TFT) with high carrier mobility as compared to organic semiconductors and transparent, flexible thin film conducting electrode (TCE) with sheet resistance comparable or even lower than low temperature deposited ITO on PET polymer will be discussed. We show that the most important SWCNT property controlling the conductivity of the SWCNT-based TCE is the nanotube bundle length.

LINEAR AUGMENTED CYLINDRICAL WAVE METHOD FOR ELECTRONIC STRUCTURE OF PERFECT AND IMPURITY NANOTUBES

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Every carbon single-walled nanotube (SWNT) can be generated by first mapping only two nearest-neighbour C atoms onto a surface of a cylinder and then using the rotational and helical symmetry operators to determine the remainder of the tubule. With account of these symmetries, we developed a symmetry-adapted version of a linear augmented cylindrical wave (LACW) method. In this case, the cells contain only two carbon atoms, and the ab initio theory becomes applicable to any SWNT independent of the number of atoms in a translational unit cell [1]. The approximations are made in the sense of muffin-tin potentials and local-density-functional theory only. We have calculated the total band structures and densities of states of the chiral and achiral, semiconducting, semimetallic, and metallic carbon SWNTs up to the (100, 99) tubule containing the 118 804 atoms per translational unit cell. About 150 functions produce convergence of the band structures better then 0.01 eV independent of the number of atoms in the translational unit cell. Moreover, the electronic structure of double-wall carbon nanotubes (DWNT) consisting of two concentric graphene cylinders is calculated in the terms of the LACW method [2]. In this approach, the electronic spectrum of the DWNTs is governed by the free movement of electron in the interatomic space of two cylindrical layers, by electron scattering on the MT spheres, and by electron tunnelling between the layers. The electronic structure of SWNTs embedded in a crystal matrix is investigated using LACW method too [3]. A delocalization of the nanotube electrons into the matrix region results in a strong band-structure perturbation. In the case of armchair nanotubes, the delocalization is responsible for a high energy shift of the states and growth of the electron density of states at the Fermi level. For the semiconducting nanotubes, it causes a decay of the minimum energy gap and the formation of a metallic state. The first-principle numerical method for calculation of the electronic structure of the impurities in the SWNTs based Green function technique is developed [4]. The host SWNTs electron Green function is calculated by using the LACW theory, the impurities being described by the single-site perturbed muffin-tin potentials in otherwise perfect nanotubes with the rotational and helical symmetries. Due to account of these symmetry properties, the method is applicable to any tubule including the chiral SWNTs with point defects. The Green function of the impurities is calculated in the terms of an algebraic Dyson equation. We give results for the boron and nitrogen impurities in carbyne and variety of the metallic and semiconducting SWNTs.

This study was supported in part by the RF BR (Grant no. 08-04-00262)
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AB INITIO ELECTRONIC BAND STRUCTURE CALCULATION OF TWO-DIMENSIONAL NANOPARTICLES OF GALLIUM SELENIDE

D.V.Rybkovskiy, I.V. Vorobyev, A.V. Osadchy, E.D. Obraztsova

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The gallium selenide nanoparticles (similar to the bulk GaSe crystals) are characterized by a strong structural anisotropy. Thus the quantum dots of this material are usually synthesized in form of thin disks [1] with a thickness of four atoms (a tetralayer). If such particle has a large diameter, its electronic properties are similar to those of the single gallium selenide tetralayer.

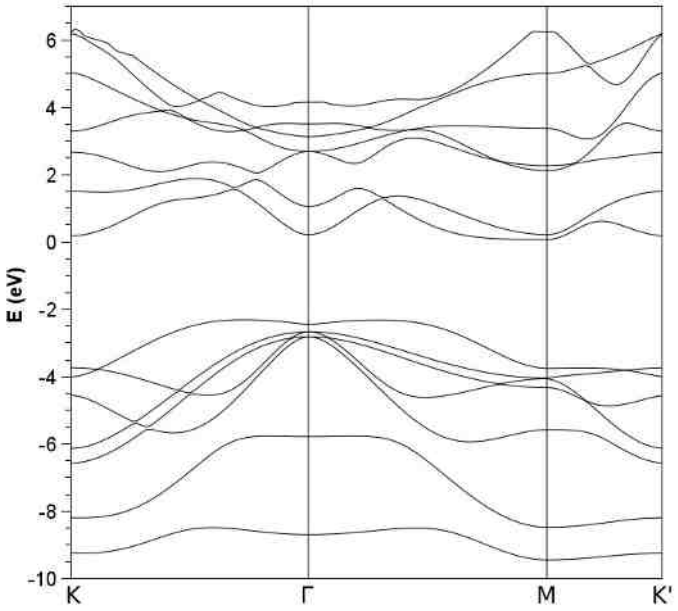

Fig.1. - Calculated energy bands for the single GaSe tetralayer.

To describe the electronic structure of these nanoobjects we have performed ab initio computation of the single and multiple GaSe tetralayers, as well as that of the bulk material. The two-dimensional electronic band structure have been obtained via the first-principles calculations based on the pseudopotential density functional theory (Fig.1). To adjust the band gap value a correction in frames of GW approximation has been made. A narrowing of the band gap for the bigger number of tetralayers has been demonstrated. The obtained information can be used in spectroscopic investigation of gallium selenide nanoparticles.

The work was supported by RFBR-09-02-91231 and federal target program "Scientific and pedagogic personnel of innovative Russia" 2009-2013 .

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INVESTIGATION OF RELATIVE STABILITY AND BAND GAP VALUE FOR ZIG-ZAG CARBON NANOTUBES

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In this work we have investigated a structural stability and electronic properties of single-walled (10,0), (19,0), (20,0), (21,0) and double-walled (10,0)@(19,0), (10,0)@(20,0), (10,0)@(21,0) carbon nanotubes (CNTs).

The energy gap, total energy and density of states were calculated with first-principles density functional theory as implemented in *Quantum ESPRESSO* code [1].

We have used an ultrasoft pseudopotential [2] for the carbon atoms and a plane-wave cutoff of 500 eV. The optimal atomic positions were determined by a convergence of a total energy with an accuracy of 0.3 meV. We have adopted a supercell model in which the CNTs considered were arranged with their adjacent outer walls separated by 10 nm.

The binding energies were calculated as the difference in total energy between the compound and a pseudoatomic calculation done for the same cutoff [3]. Obtained binding energies for graphite, largest single-walled CNT and largest double-walled CNT are 9.50 eV, 8.99 eV and 8.96 eV respectively.

The results indicate that the single-walled CNTs are more stable than the double-walled ones (Fig.1). But both of them are energetically less favorable than a bulk graphite.

The thinnest of the considered single-walled CNTs have shown an energy gap about 0.75 eV, while the single-walled CNTs with the largest diameter should have an energy gap about of 0.35 eV.

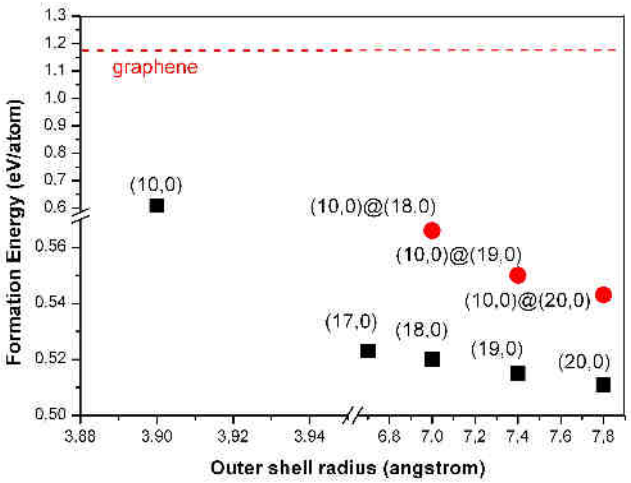

Fig. 1. Formation energy per atom as a function of nanotube radius.

The energy gap of the largest double-walled CNT (10,0)@(20,0) is 0.48 eV, that is slightly different from the gap of the outer shell. This fact can be explained by a slight interwall interaction.

This work was supported by RFBR-09-02-00792 project and by the Russian President Grant (MK-1614.2009.2).

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FABRICATION AND DETECTION OF A GRAPHENE MECHANICAL RESONATOR

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We present a new technique to make a suspended graphene as a mechanical resonator, and an electrical method to detect its resonance. The graphene sheet is transferred and assembled onto a prefabricated gate electrode. The suspended graphene is actuated by applying an AC driving voltage, resulting in a time-varying capacitor between the graphene and the gate. An injected RF signal is modulated by the time-varying capacitor, and the reflected sideband signal is detected to find the mechanical resonance of the graphene. Our fully electrical detection method is applicable for nanoscale mechanical resonators in a large frequency range. The fabrication method is promising to build more complex nanoelectromechanical systems from graphemes or carbon nanotubes.

CNT-METAL INTERCONNECT ELECTRONIC STRUCTURE CALCULATIONS AND RESISTIVITY SIMULATION

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Cluster approach based on the multiple scattering theory formalism, realistic analytical and coherent potentials, as well as effective medium approximation (EMA-CPA), can be effectively used for nano-sized systems modeling. This allows us to calculate the dispersion law $E(k)$, electronic density of states, conductivity, *etc*. The multiple scattering problems are stated for radial (*e.g.,* quantum dots) and axial (*e.g.,* nanowires, nanotubes) symmetry approaches**.**

Basic attention is paid now for applications on carbon nanotubes (CNTs) of various morphology which possess the unique physical properties in nanoelectronics, *e.g.*, contacts of CNTs with other conducting elements of a nanocircuit which can be promising candidates for interconnects in a high-speed electronics. The main problems solving for resistance in CNT junctions with metal particles appear due to the influence of chirality effects in interconnects of single-wall (SW) and multi-wall (MW) CNTs with the fitting metals (Me= Ni, Cu, Ag, Pd, Pt, Au) for predefined CNT geometry. Using the developed model of *'effective bonds'* in the framework of presented approach and Landauer theory, we can predict the resistivity properties for both SW and MW CNT-Me interconnects. We have also developed the model of the inter-wall interaction inside the MW CNTs, which demonstrates possible 'radial current' losses [1].

Special attention is devoted to simulation of frequency and temperature properties CMT-Metal interconnects.

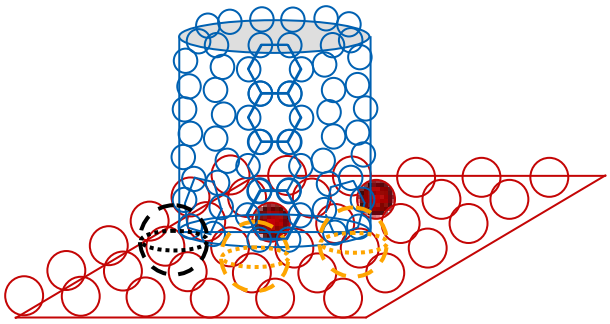

Figure 1. Model of 'active bonds'for CNT-Metal Interconnect

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ELECTROMAGNETIC RESPONSE OF NANOCARBON BASED EPOXY COMPOSITES: MICROWAVE AND LOW-FREQUENCY ANALYSIS

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The problem of the design and fabrication of effective low-cost electromagnetic coatings for microwave frequencies became pressing nowadays, because of wide dissemination of their applications, in particular for targeting radars and vehicle speed detection (Ka-band, 26-37 GHz). Here we focus on the comparative study of electromagnetic response properties provided by different forms of nanocarbon in Ka-band, such as carbon black (CB) and single-walled and multi-walled carbon nanotubes incorporated into the epoxy resin in small percentage (0.5 wt.%).

Microwave probing was provided in the 26-37GHz range by the scalar network analyzer. The cured specimens were cut precisely to the waveguide cross-section 7.2×3.4 mm. S-parameters were measured by subsequent inserting specimen into the waveguide. The measurements were performed with free-standing polymer films.

It has been shown that inclusion of carbon black does not impact significantly the electromagnetic (EM) response properties. In contract to CB, inclusion of 0.5 wt.% of carbon nanotubes (both single-walled and multi-walled ones, SWNT and MWNT) leads to the significant rise of the absorption and the reflection ability of the epoxy resin composites.

That has been supported by the low-frequency data (20Hz-1MHz). It has been demonstrated that the complex dielectric permittivity and electric conductivity of the CB based nanocomposite are similar to those of the epoxy resin alone, used as a control specimen, whereas the conductivity of SWNT composites turns out to be 6 orders of magnitude higher than the resin alone. In MWNT composites the conductivity shows 2 orders of magnitude enhancement. The corresponding increase of the permittivity is about 4 and 2 orders of magnitude for SWNT and MWNT inclusions, respectively.

Acknowledgements
The research has been supported by ISTC project B-1708, NATO PST.CLG.983910 and EU FP7 CACOMEL project FP7-247007.

ELECTRICAL PROPAGATION MODELS FOR SINGLE- AND MULTI-WALL CARBON NANOTUBES

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Because of their unique electrical, mechanical and thermal properties, carbon nanotubes (CNTs) are emerging materials recently proposed (*e.g.*,[1]) in nanoelectronics applications (*e.g.*, interconnects, antennas, transistors, passives, resonators,...). The electromagnetic and circuital modelling of such materials is a task of fundamental importance in view of the implementation of tools for design and verification of such nanoscale systems. An accurate modelling of the CNT electrodynamics requires, in principle, a quantum mechanical approach; on the other hand, the electromagnetic and circuital models should result simple enough to obtain simulation tools useful for analyzing real-world applications. The recent literature proposes different models, either based on phenomenological approach and on semi-analytical one ([2]-[5]).
In this paper we present a rigorous electrodynamical model which describes the charge carriers in CNT as an electron fluid composed of many electron species differing between them for the effective mass, which takes into account for the interaction with the nanotube ion lattice. The hydrodynamic equations are derived in a self-consistent way from the semi-classical Boltzmann equation, leading to a linear transport model for the electrons. The model may be applied to CNTs of arbitrary chirality, either metallic or semiconducting, at microwave through terahertz frequencies, and may be extended to the case of multi-wall CNTs.
Using this model, a CNT constitutive equation in frequency domain is derived and coupled to the classical Maxwell equations. Assuming the electrical propagation to be of quasi-TEM type, a circuit model is then derived in the frame of the transmission line theory, where the classical electromagnetic per-unit-length parameters are modified to take into account the presence of kinetic and quantistic phenomena. The circuital model generalizes the existing ones, since it includes the effects of CNT size, chirality and temperature and is extended to bundles of either single-wall and multi-wall CNTs.

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GRAPHENE AND NANOTUBE PHOTONICS

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The richness of optical and electronic properties of graphene attracts enormous interest. Graphene has high mobility and optical transparency, in addition to flexibility, robustness and environmental stability. So far, the main focus has been on fundamental physics and electronic devices.
However, we believe its true potential to be in photonics and optoelectronics, where the combination of its unique optical and electronic properties can be fully exploited, the absence of a bandgap can be beneficial, and the linear dispersion of the Dirac electrons enables ultra-wide-band tunability. The rise of graphene in photonics and optoelectronics is shown by several recent results, ranging from solar cells and light emitting devices, to touch screens, photodetectors and ultrafast lasers. Despite being a single atom thick, graphene can be optically visualized [1]. Its transmittance can be expressed in terms of the fine structure constant [2]. The linear dispersion of the Dirac electrons enables broadband applications. Saturable absorption is observed as a consequence of Pauli blocking [3,4]. Chemical and physical treatments enable luminescence [5]. Broadband luminescence is also observed upon ultrafast laser irradiation. We will report the linear and nonlinear optical characterization of graphene-polymer composites prepared using wet chemistry techniques [3-5]. The composites are then integrated in a fiber laser cavity, to generate ultrafast pulses. We obtain pulse durations as short as 200fs capable of broadband tunability [3,4]. These composites could mode-lock from visible to IR due to the linear dispersion of Dirac electrons.
Carbon nanotubes (CNTs) are excellent saturable absorbers, i.e. they become transparent under sufficiently intense light [3,6-11]. This has great potential for applications in photonics. By tuning the nanotube diameter it is easy to cover a broad optical range of interest for telecommunications, medicine and military applications [9]. CNT saturable absorbers can be produced by cheap wet chemistry. These are successfully used to mode-lock lasers in a broad spectral range [6-11], with pulse widths as short as 90fs [11] and output power exceeding 1.6 W [10], orders of magnitude higher than previous CNT-based fibre lasers.

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New approaches in formation of nanocarbon non-linear optical elements

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Last five years have demonstrated a high potential of single-wall carbon nanotubes (SWNTs) for application in non-linear optics. From the idea of possibility to use a "carbon nanotube+polymer" composite as a saturable absorber for solid state lasers (including the fiber ones) (Fig.1-1) [1,2] we came today to semi-industrial developments of carbon nanotube-based elements for formation of femto-second output laser pulses.

The bulk elements (instead of films) are needed today for formation of all-fiber lasers and, hopefully, for realization of an active (generation) regime in lasers. Here a big step ahead is a success with a mode-locking realization with *holey fibers* filled with SWNT suspension. After drying it forms a thin film of SWNTs onto the walls of holes. The resonator characteristics can be modified by choosing the length of a holey fiber piece (Fig.1-2) [3]. The sub-picosecond output pulses have been obtained.

Recently another nanocarbon material – graphene- has shown its efficiency in mode-locking [4]. Its unique advantage is an almost endless spectral working range. The graphene saturable absorbers can be formed for lasers which never demonstrated mode-locking before. In our case we used the CVD-grown flakes with a few graphene layers (Fig.1-3) [5] for mode-lockers provided the output pulses with duration about 600 fs.

The work was supported by RFBR project 10-02-00792 and RAS research programs.

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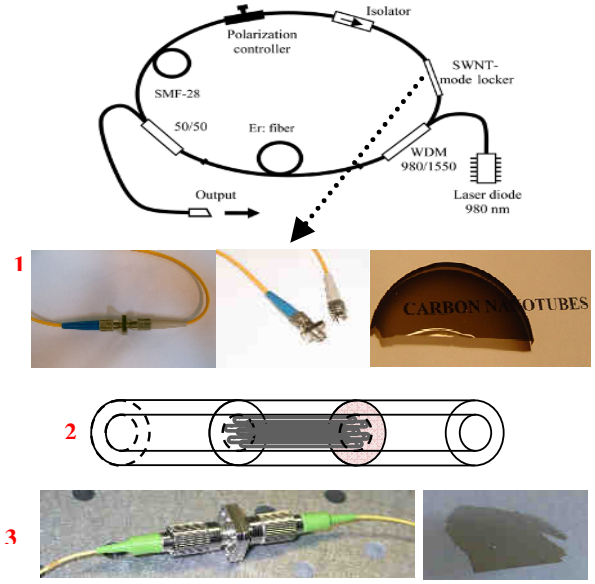

Figure 1. *The nanocarbon-based saturable absorbers for Er fiber lasers in form of:* ***1*** *– a polymer film with embedded SWNTs,* ***2****- a piece of a holey fiber with a thin film of SWNTs on the hole walls(after drying) ,* ***3****- a film containing a few layers of graphene.*

Photoexcitation dynamics in Carbon Nanotubes

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Carbon nanotubes (CNT) have promising features for their use in optoelectronics like, narrow optical resonances, ultrafast nonlinear response and ballistic 1D charge transport. They have π-electrons delocalized along the surface in quasi 1D electronic states. Low energy optical transitions reach correlated states, often described as 1D Wannier-Mott excitons, few nanometers in size[i] and responsible for narrow spectral lines and generally weak emission. Solid state networks of CNTs, containing a broad distribution of tube diameters and chiralities, engender the near future potential for technological applications. In order to predict favourable optoelectronic performances of such networks, both the intra tube and the inter-tube dynamics must be known in detail. This talk regards time resolved pump-probe experiments in sample of different composition, aimed at understanding such dynamics. A tutorial introduction on the technique will be followed by the presentation of recent results including excitation relaxation in semiconducting and metallic[ii] tubes and coherent phonons dynamics[iii]. In the introduction the pump-probe signal will be described within the effective linear approximation and then according to the third order perturbation theory for the two level systems. Coherent phonons will be described at phenomenological level. These notions will then be applied to the analysis of results onto chiral enriched sample (dominant (6,5) tube), small bundles and conjugated polymer/nanotubes blends.

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Electronic structure of SWCNTs at DFT level and beyond: New insight from Raman, optical, and electron spin resonance experiments.

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In a first approximation the electronic structure of SWCNTs has been described reasonably well in a tight binding or in an extended tight binding picture, starting from the graphene structure. This approximation fails if curvature effects lead to substantial σ-π overlap and if electron correlation becomes important. The former effect is particularly relevant for tubes in the diameter range between 0.5 and 1 nm. Electron correlation is strongly enhanced in the tube system due to the 1D character of the electrons. In semiconducting SWCNTs electron correlation leads to an increase of the energy gap on the one side and on the other side to a reduction of the lowest optical transition due to dominating exciton transitions. Due to the opposite sign of the two latter effects DFT can still yield a reasonable good agreement with experiment.

In this presentation we analyze the electronic and vibrational structure of SWCNTs with ultra high curvature which demonstrates the dramatic differences between theoretical results obtained from tight binding and from DFT. Tubes with diameters down to 0.405 nm were investigated by resonance Raman scattering and transmission electron microscopy. Stability of these ultrahigh curvature tubes was guaranteed as they were grown inside of HiPco tubes which had a diameter of only 1.1 nm. Optical transition energies were evaluated including correlation effects as demonstrated by Arujio et al. [1].

Unexpected behavior was also observed for the dispersion of the D-line and for the dispersion of the 2D line of SWCNTs with 0.7 nm diameters. These high curvature tubes exhibit a much smaller dispersion than the conventional 1.4 nm tubes with the consequence of a cross over of the dispersion line for the two sets of tubes. This was evidenced from 13C isotope labeled material.

For fully semiconductor-metal separated tubes dramatic differences in the Raman and resonance Raman response were observed when DWCNTs were grown from the different starting materials. These experiments reveal also indications for a different Van der Waals interaction between semiconducting and metallic tubes.

Fully semiconductor-metal separated tubes grown from a nonmagnetic catalyst allowed for the first time to obtain reliable ESR date for the two electronically very different sets of samples. Among others the experiments on the metallic samples revealed the opening of a gap at very low temperatures around 3 K. The magnitude of the gap is of the order of 0.3 meV and was observed for tubes with a mean diameter of 1.6 nm. It is suggestive to correlate this gap to the opening of a gap at slightly higher temperatures of 20 K as observed by NMR for tubes with a much smaller diameter of only 0.7 nm [2]. In both cases the opening of the gap is suggested to originate from Coulomb correlation as Coulomb correlations is expected to scale inverse to the size of the tubes.

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ELECTROLUMINESCENCE OF CARBON NANOTUBE – CADMIUM SULFIDE NANOPARTICLE HYBRIDS

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At present the development of hybrid nanosystems combining the properties of one-dimensional carbon nanotubes (CNTs) and quantum dots from semiconducting materials attracts considerable interest. Interaction of semiconducting nanoparticles with light is expected to have result in the electron photocurrent through the CNT and localization of the hole on the nanoparticle that should allow creating a new type of photovoltaic devices. Here, we present a preparation and investigation of hybrid materials from CNT and CdS nanoparticles.

CdS nanoparticles were grown on the surface of aligned multi-walled CNTs from an aqueous solution of $CdCl_2$, $(NH_2)_2CS$ (Thio), and NH_3. Scanning electron microscopy showed that size of the nanoparticles can vary from 5 to 100 nm. The synthesis conditions allow preserving alignment of CNTs in the array and uniform decorating the CNTs with CdS nanoparticles. The structure of the CdS nanoparticles was studied using high-resolution transmission electron microscopy. The electron diffraction carried out for different CdS nanoparticles showed the formation of hexagonal crystal lattice. Continuous CdS/CNT interface indicates that nucleation and growth of the nanoparticles take place directly on the nanotube surface. Electronic state of elements in CdS/CNT hybrid material was examined using x-ray photoelectron spectroscopy (XPS). The shift of binding energy of Cd $3d_{5/2}$ and S $2p_{3/2}$ lines was detected compared to the bulk CdS. XPS evidences that the formed CdS particles have the oxidized outer layer that is probably related with reactions conducting in basic solution in the process of the nanoparticle growth.

Electroluminescence properties of CdS nanoparticles deposited at the CNT tips were measured in the conditions of field electron emission from the CNT array. ITO glass was used as an anode and image was taken with a photocamera. Images exhibited a set of luminous points corresponding to individual CdS nanoparticles, which are probably deposited on the CNT tips. The points were green and red coloured and different colouring could be related with different size of the nanoparticles.

OPTICAL ABSORBTION MODE REDISTRIBUTION IN CARBON NANOTUBES SYNTHESIZED FROM DOPANT-CONTAINING CATALYTIC MIXTURES

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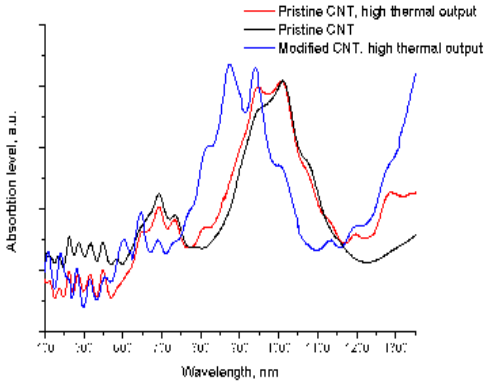
Single walled carbon nanotubes are well-known both for their chirality-dependent electronic properties and stochastic behavior of those. The latter is the main obstacle on the way of widespread use of carbon nanotubes in electronical and optical applications. It lead to development of many sophisticated tecniques aimed at separation of required fractions of carbon nanotubes from as-synthesized material.

Doping of the carbon SWNT can modify their electronic properties to suit particular needs. In our experiments an arc-discharge technique has been used to produce the modified carbon SWNTs. Two approaches have been realized: with a varied concentration of the dopant source [1], and with a varied thermal output. For the second approach the Raman spectroscopy has confirmed changes in the phonon structure of the synthesized material [2].

While the Raman spectroscopy is a very sensitive instrument for the phonon structure analysis, an optical absorption spectroscopy allows a direct observation of the band gap of the macroscopic amount of the synthesized material (see figure). Carbon SWNTs synthesized in helium atmosphere from the catalytic mixture modified with 5% (by mass) of BN and 5% B_4C using a high thermal output in the arc (4 kW) show a "blue" band gap shift. The atmosphere of nitrogen has also been used.



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PHOTOVOLTAIC CONVERSION FACTOR DEPENDENCE ON LASER POLARIZATION FOR NANOCARBON FILMS

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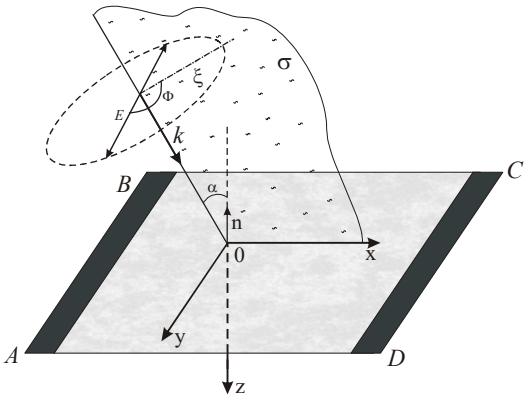
Pulsed laser radiation conversion into dc voltage has been demonstrated recently in nanographitic materials and carbon nanotube yarns [1, 2]. The phenomenon has been described in terms of optical rectification effect [1] and photon drag effect [2]. The photovoltaic properties of the carbon materials have been characterized by the conversion factor η which depends essentially on incident angle α of the laser beam in respect of sample surfaces as $\eta = F(\alpha)\times\sin 2\alpha$ (where $F(\alpha)$ is a function varying slowly with α). In this report we present further investigation of the photovoltaic effect directed on determination of dependence of η on laser polarization (which is characterized by the angle Φ between the plane of light incidence and electrical vector of the laser radiation).

The dependencies of η_x, η_y on Φ were determined experimentally for two different experimental setups respectively: 1) with two electrodes *AB* and *CD* lying in parallel to the plane of light incidence σ and with axis O*X* of the rectangular coordinate system *XYZ* directed perpendicular to the electrodes (see in Figure); 2) with the electrodes *AB* and *CD* lying perpendicular to the plane σ and with the axis *x* directed parallel to the electrodes.



It was found for the nanocarbon films (25×25 mm) that η_x and η_y obey the following dependencies:

$$\eta_x = \eta_x^0 \times F_x(\alpha,\Phi)\times(c+\cos 2\Phi),$$

$$\eta_y = \eta_y^0 \times F_y(\alpha,\Phi)\times\sin 2\Phi,$$

where $\eta_x^0 = 24.5$ mV/MW; $c = 2.35$; $\eta_y^0 = 43.7$ mV/MW; and $F_x(\alpha,\Phi)$, $F_y(\alpha,\Phi)$ are even functions of α vanishing at α = 0, ±90°.

The presented experimental results explained by excitation of surface current due to quasi-momentum transfer from photons to electrons and by surface photo-galvanic effect.

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CHARACTERIZATION OF NANOGRAPHITE FILMS BY SPECULAR GLOSS MEASUREMENTS

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Ability to scatter light is one of the most important properties that allow one to assess the quality of a surface. The quantitative measure of this ability is the specular gloss *G,* which is defined by international standards ASTM D523 and ISO 2813 as

$$G = 100 \times \frac{I_S}{I_{Ref}}, \qquad (1)$$

where I_S and I_{Ref} are irradiances reflected from the surface in question and reference (usually a highly polished black glass), respectively, at specific angle of incidence. The specular gloss depends on the variation of refractive index and surface roughness. However situation becomes more complicated when one need to assess the quality of films of subwavelength thickness. In such a case effects of surface roughness and inhomogeneity of the refractive index are usually difficult to visualize using conventional glossmeters. Here we demonstrate that quality of ultrathin graphite films on Ni substrate can be characterized by measuring gloss map of the sample with a diffractive optical glossmeter (DOG), which the analyses the 4 × 4 light dot interference matrix created by a diffractive optical element described more detail in Ref [1].

In our experiment, 10-20 nm thick graphite films were grown by plasma assisted chemical vapour depositing (CVD) process in a 10 mm × 10 mm × 1 mm Ni substrate [2] and characterized with the DOG. The gloss maps for two obtained films are shown in Fig 1. One can observe that DOG allows us to quantify the quality of the film showing variation of its morphology and optical homogeneity.

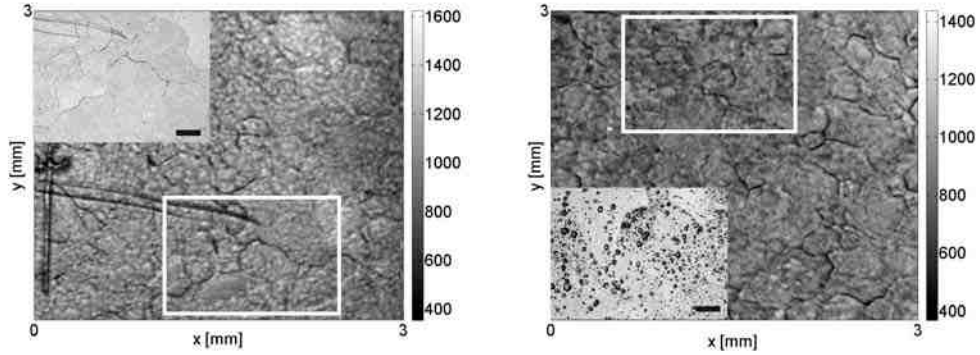

Figure 1. Glossmaps of two nanographite films on Ni substrates. One can observe that avrerage gloss of the sample (a) is about 200 Gloss Units (GU) higher than that of the sample (b) indicating the difference in the nanographite film quality. Insets show images of the selected areas obtained with optical microcope (inset scale bar is 200 μm).

In conclusion, we demonstrate that the DOG technique can be employed for qualitative characterisation of the large ultrathin graphite films on a metal substrate. The developed technique can be employed to visualize morphology and to estimate the number of graphene layers on both metal and dielectric substrate.

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TERAHERTZ EMISSION FROM NANOCARBON AND GRAPHITE FILMS

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Nanocarbon structures and graphite have attracted a great deal of attention because of the peculiar carrier dynamics. Recently, photon drag effect in nanocarbon film has been reported [1], and this current is expected to be a novel terahertz (THz) radiation source.

Here, we observed THz emission from nanocarbon film and thin graphite film by pumping with femtosecond pulsed laser. From the results of pump power dependence and pump polarization dependence, THz emission is explained by photon drag effect.

Figure 1 shows the schematic picture of experiment. Two types of samples are prepared. Sample A is nanocarbon film that consists of graphite nanosized crystallites (5-50 graphite sheets and few microns long). Film is grown using the chemical vapor deposition (CVD) techinique on Si substrate [2]. Sample B is thin film graphite (approximately 50 sheets, multi-domain) which was placed on glass substrate after the CVD growth on Ni substrate [3]. A regenerative amplified Ti:sapphire laser (120 kHz, 800 nm, 200 fs) is used as a light source. The incident angle of pump beam is 45°, and THz electric field in reflection direction is detected by electro-optic sampling, with changing the polarization of pump beam.

Since the measured THz signal was proportional to pump power, this process is second-order. This result can be explained in terms of the photon drag effect, $J_i = 2\mathrm{Re}\{\chi_{ijlm}(\nabla_m E_j)E_l^*\}$, where J is current density and χ is the relevant susceptibility tensor of the nanocarbon film. In Fig. 2, our analysis showed that a weak polarization dependence of the THz signal emitted from the sample A indicates that this film is in-plane isotropic. In contrast, the sample B possesses well-defined hexagonal symmetry of graphene that manifests itself in the pronounced dependence of the THz signal on the polarization of incident beam. Our results indicate that THz emission from bulk graphite and nanocarbon films may be governed by different microscopic mechanisms [4].

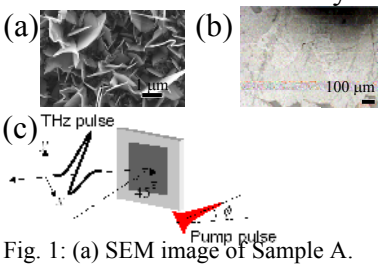

Fig. 1: (a) SEM image of Sample A.
(b) Optical microscope image of Sample B.
(c) Schematics of measurement.

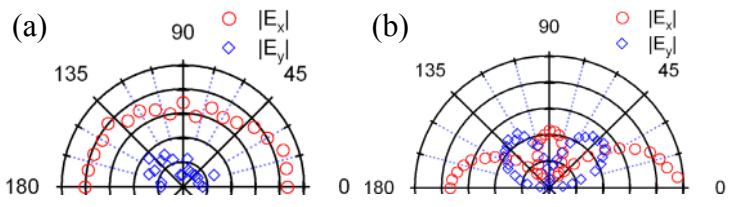

Fig. 2: Results of pump polarization dependence of THz radiation from (a) Sample A, and (b) Sample B.

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FAST SATURABLE ABSORPTION IN MULTILAYERED GRAPHENE

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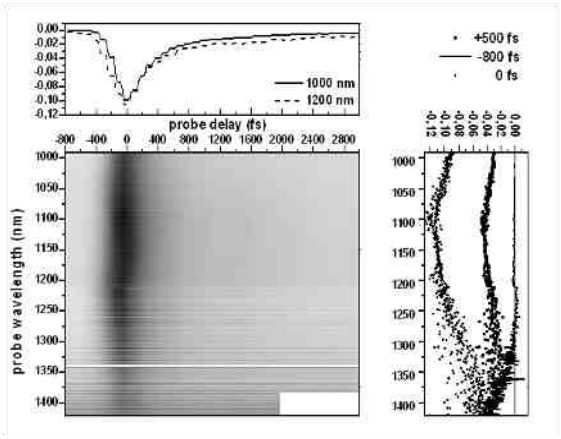
An outstanding optical and electronic properties of graphene [1] and graphene-based materials are of a great interest for photonics and for fabrication of optical devices. This is in particular due to unusual band structure of graphene and its ultra-high electron mobility that make optical properties of this material practically wavelength insensitive. Strong optical nonlinearity and subpicosecond relaxation times [2] allow one to use graphene based materials for laser modelocking [3,4] and for optical switchers operating in a wide spectral range.

Here we present broadband study of ultrafast light induced absorbance changes in thin films consists of different number of atomic layers (graphene). Time-resolved pump-probe measurements of light-induced absorbance change in thin films were carried out with 150 fs laser in near-IR spectral range (probe range: 900-1600 nm, pump range: 1100-1650 nm). Dependences of saturable absorption signal level and relaxation dynamics on pump wavelength, energy and number of grapheme layers are obtained.



Our measurements reveal the characteristic times of the fast non-linear response vary from 200 fs to 500 fs. The dynamics and amplitude of light induced absorbance change are slightly depending on pump and probe wavelengths. Linear dependence on pump energy corresponds to third order non-linear process. The third-order susceptibility for investigated samples is obtained about 10^{-11} esu.

The results of performed study confirm strong potential of graphene materials for laser applications.

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ULTRAFAST KINETICS OF PHOTOEXCITATION IN SWNT-BASED SATURABLE ABSORBERS

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The achievements of the last years in carbon nanotubes production and processing have revealed new properties of this material attractive for applications in non-linear optics and optoelectronics. Besides known before unique mechanical, electronic and chemical properties single-wall carbon nanotubes (SWNT) exhibit high-speed non-linear optical properties such as third-order optical nonlinearity and saturable absorption. In this regard a number of groups have started their studies on SWNTs employment as saturable absorbers with ultrafast recovery times. The potential of this material for passive mode-locking and Q-switch has been demonstrated for a row of fiber and solid-state lasers [1-3]. The dependency of the SWNTs absorption band on their diameter makes this saturable absorbres applicable through a wide spectral range. However up to now it is not clear what are the best nanotube parameters, sample preparation technique, setup configuration and operation wavelengths for the most efficient carbon nanotubes use in photonics.

In this work we used the ultrafast optical spectroscopy to measure the carrier relaxation dynamics in SWNTs samples prepared in different ways. We demonstrate that the surrounding matrix and the bundling grade of SWNTs in the sample affects the photoexcitation lifetimes. We have also analyzed the spectral changes in the time-development of the saturable absorption signal. We suppose that our results should be taken into account for improving the efficiency and temporal characteristics of the carbon nanotube-based saturable absorbers.

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The work was supported by the European Commission (grant number MRTN-CT-2006-035859), RFBR and RAS projects and RF president grant for young scientists MK-2921.2010.2

TRANSPARENT METALLIC AND SEMICONDUCTING FILMS BASED ON SINGLE-WALL CARBON NANOTUBES

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Single-wall carbon nanotube (SWNT) can be described as a rolled graphene sheet. Depending on the diameter and the way of rolling up the carbon nanotube can become either a metal or a semiconductor with a variable band gap.

SWNTs have many unique properties. It is a very promising material for nanoelectronics. But the main limiting factor for wide applications of carbon nanotubes in many fields always was a possibility to separate the synthesised material containing a nanotube mixture into the nanotube fractions with identical diameters or electronic properties.

Recently, new approaches were applied for a quick and efficient separation of SWNTs [1,2]. In this work we present the transparent metallic and semiconducting films formed on the base of separated SWNTs (Fig.1).

The nanotubes used for formation of transparent films have been separated by a density gradient ultracentrifugation [1,3]. The films have been deposited on quartz substrates and investigated by optical spectroscopy (UV-VIS-NIR absorption, Raman spectroscopy and photoluminescence).

The work was supported by RFBR-09-02-01051 and RFBR-09-02-91076 projects.

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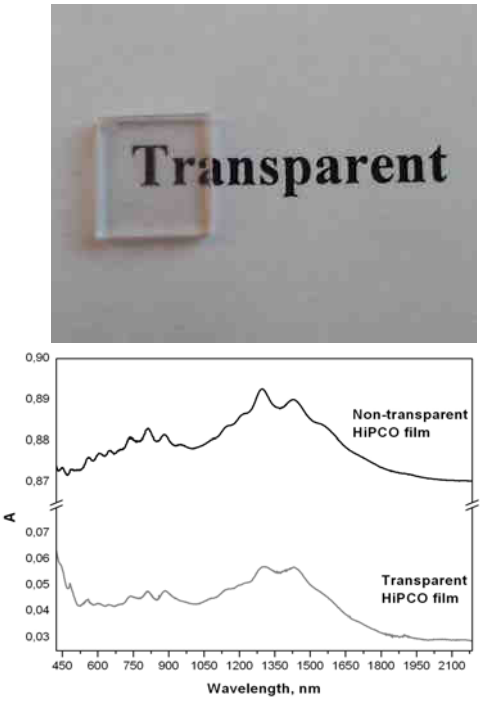

Fig.1. *A photo of the transparent metallic SWNT film deposited on quartz substrate and UV-VIS-NIR optical absorption spectra of transparent and non-transparent films.*

Poster session I

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AB-INITIO INVESTIGATION OF ELECTRONIC PROPERTIES OF DOUBLE-WALL CARBON NANOTUBES

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Unique properties of carbon nanomaterials, resulting from their quantum dimensions, attract an essential attention of researchers.

In this paper we represent the results of *ab-initio* computer modeling of electronic dispersion dependencies and density of electronic states (DOS) for single and double wall carbon nanotubes. The density functional theory with a pseudo-potential method has been used for the calculations.

The DOS of double wall carbon nanotubes contains peaks corresponding to peaks of every inner and outer tubes. The interlayer interactions leads to peak position shift.

Also the electron density for highest occupied and lowest unoccupied level has been calculated (Fig. 1,2) The calculations shown that the electronic density for lowest unoccupied level localized on outer nanotube.

This work was supported by RFBR grants and Russian President Grant (MK-1614.2009.2).

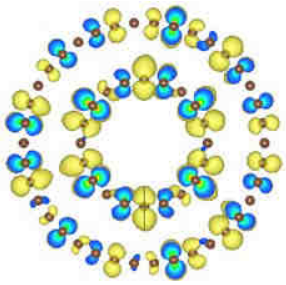

Fig. 1

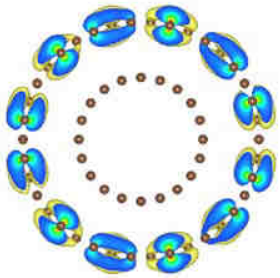

Fig. 2

Study of single-wall carbon nanotubes film grown by ethanol chemical vapor deposition process

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Single-wall carbon nanotube films were produced by an alcohol chemical vapor deposition (CVD) process with an ethanol as a source of carbon [1]. Nanotube films were produced in a low-temperature process (in the temperature range 750 – 850^{o}C). A quartz substrate was dipped into a catalytic solution containing Co/Mo for formation of metal nanoparticles on the quartz surface. The polished quartz slabs were used for single-wall carbon nanotube grown. It was necessary for application of nanotubes in optical tasks.

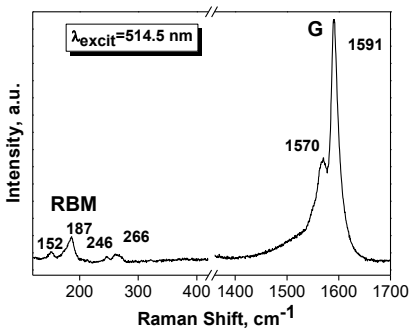

Fig.1. Raman spectra of SWCNTs on quartz surface registered with a laser excitation 514.5 nm.

The nanotube films synthesized were investigated by optical spectroscopy and electron microscopy techniques. A Raman spectroscopy was used as a main spectroscopic technique (Fig.1). The Raman spectra of nanotubes were obtained with the different excitation wavelength ranging from 476 nm to 647 nm. The nanotube diameter distribution has been estimated and the diameters corresponding to semi-conductor and metallic nanotubes have been assigned.

A scanning electron microscopy was used as a main microscopy technique. The technique allowed getting an overview of the nanotube films grown. As a result, a non-homogeneity of the metal catalyst nanoparticles deposited from the catalytic solution has been revealed.

These two methods have allowed quite a comprehensive characterization of the nanotube films grown with the ethanol CVD process. The films containing the semi-conductor and metallic SWCNTs with diameters in a wide range have been deposited. A nanotube growth mechanism has been proposed.

The work was supported by RFBR-10-02-00792 and RAS research project "New materials".

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MODERNIZED *Z*-SCAN TECHNIQUE FOR INVESTIGATION INFLUENCE OF NONLINEAR LIGHT SCATTERING ON OPTICAL LIMITING IN NANOCARBON SUSPENSIONS

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It is well known that suspensions of various carbon nanoparticles exhibit the phenomenon of optical limiting (OL). This effect can be used to create various devices and protect photosensitive objects from destructive action of high-power light fluxes. Conventionally, the optical limiting is studied using the so-called *z*-scanning technique, according to which the optical transmission coefficient of a cell with suspension is measured for various positions of the waist of a focused laser beam. In spite of the many reports on OL, no experiments aimed at correlating the reduction in transmission to the increase in scattered light intensity in *z*-scan measurements have been described in the literature until our fresh publication [1]. Here we present the detail descriptions of original modernized *z*-scan technique **(**Figure**)** permitting to investigate influence of nonlinear light scattering on optical limiting in nanocarbon suspensions.

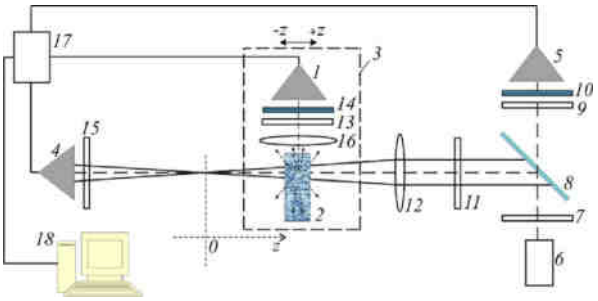

Figure. Experimental arrangement for modernized *z*-scan measurements:
1, *4*, *5* – light sensors; *2* – cell filled with the suspension; *3* – positioning stage; *6* – laser; *7*, *13* – infrared filters; *8* – mirror; *9*, *11*, *15* – neutral filters; *10*, *14* – ground glass; *12* – collecting lens; *16* – collimating lens; *17* – pulse energy measurements system; *18* – computer.

The setup presented in Figure differs fundamentally from known configurations in that the light sensor *1* and the cell containing the suspension *2* are mounted directly on the positioning stage *3* so that, in the course of *z*-scan measurements, the active area of the sensor is always opposite to the lateral side of the cell. This allowed us to monitor the energy, amplitude and temporal characteristics of the 90^0 – scattered laser light while moving the cell along the optical axis *z*, with the origin at the laser beam waist. The incident and transmitted laser pulses were detected by sensors *5* and *4*. Thus we could monitor parameters both transmitted and 90^0 – scattered laser pulses while moving the cell along the optical axis *z*.

Application of this modernized *z*-scan technique allowed us to establish that OL in aqueous CNT suspensions and nanodiamond hydrosol is mainly due to nonlinear scattering.

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TERAHERZ PROBING OF NANOCARBON BASED EPOXY COMPOSITES

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This communication presents the study of spectral features of nanocarbon based epoxy resin composites in the terahertz frequencies (0.2-18THz) where the search of new operational materials and components is of particular importance for various promising applications. The series of pre-percolative carbon black (CB) and close-to-percolation threshold carbon nanotubes (CNT) samples made in seven different thicknesses with the same small content of nanocarbon (0.5 wt.%) were prepared using poxy resin Epikote 828 by Hexion Company. The types of fillers used, were:

- *commercial Multi-Wall CNTs (MWNTs), Purity: 95%+, Diameter: 20–40 nm and Length : 0.5 – 200 μm;*
- *Commercial Single-Wall CNTs (SWNTs), Purity: 90%+, Average Diameter: 1.5nm and Length :10 - 20 μm;*
- *Commercial Carbon Black Printex90 Evonik Degussa.*

A high THz attenuation ability is demonstrated by the CNT-based samples, especially by single-walled CNT. The transmission at 1 THz trough the sample containing 0.5 wt.% of SWNT inclusions is 12 times less then trough pure resin, and 3 times less in case of MWNT incorporation. The effect of CB in small concentration is close to the net resin.

In the IR frequency range (from 3 to 18 THz) the small reflection of THz signal were observed (up to 5%) for all types of nanocarbon inclusions. The maximal reflection is demonstrated by the net epoxy resin, which means strong screening effect of the given matrix.

A theoretical interpretation of the resonance behavior demonstrated by CNT-based samples is given using the nanoelectromagnetics [1] utilizing the theory of antenna-like THz behavior of isolated carbon nanotubes predicted in Ref. [2].

Acknowledgements
The research has been supported by ISTC project B-1708, NATO project PST.CLG.983910 and EU FP7 CACOMEL project FP7-247007.

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TEMPERATURE INFLUENCE ON FIELD ELCTRON EMISSION FROM NANOGRAPHITE FILMS

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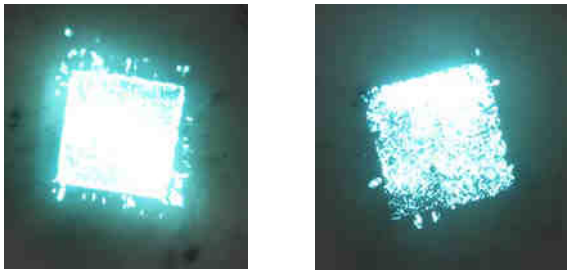
Investigation of structural and emission properties of nanographite films (NGF) obtained by chemical vapor deposition (CVD) are presented. As was shown before NGF with its efficient low field electron emission proved to be a promising material for vacuum electronics application [1-3]. The technology of electron device production is a complex process and includes different stages of manipulation. Heating is among them and its influence on the film properties is unknown. Undoubtedly study of the films properties modification due to the temperature variation is useful to investigate their applicability.

In order to explore the temperature influence on the films obtained by chemical vapor deposition few series of samples were synthesized and characterized. The samples were heated in the atmosphere air in the range of temperatures from 200 to 700^{0}C.

Comparative study by Raman spectroscopy, SEM and current voltage measurement were performed to analyze the structural and emission changes of NGF. The films don't show any considerable changes of emission properties (fig.1) up to the temperature 625^{0}C meanwhile electron microscopy (fig.2) shows structure changes. Higher temperature treatment causes film peeling from the substrate and emission downgrade.



a b

Fig. 1. Emitting centers location before (a) and after (b) 625^{0}C temperature influence.

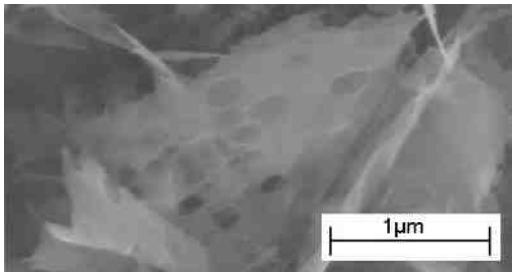


Fig. 2. Electron microscope image of the film influenced with 660^{0}C.

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EFFECT OF CVD PROCESS PARAMETERS ON SHAPE OF DIAMOND CRYSTALLITES

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Polycrystalline diamond films produced by chemical vapor deposition are attractive for many applications. The physical properties of the CVD diamond depend essentially on structural and morphology characteristics of crystallites composing the films. Here we present results of experimental studies of effect of the CVD process parameters on shape of obtained diamond crystallites. The diamond growth has been performed on silicon substrates in hydrogen-methane gas mixture activated by a dc gas discharge [1]. The quantitative characterization for the shape dependencies were made for a microscopic growth parameter $\boldsymbol{\alpha}=\sqrt{3}V_{111}/V_{100}$, where V_{111} and V_{100} are growth rates in <111> and <100> directions, correspondingly. The parameter $\boldsymbol{\alpha}$ was measured using scanning electron microscopy (SEM) images of the diamond crystallites grown at different substrate temperatures and methane concentrations in the gas mixture. To provide growth of individual crystallites we use the processes with short durations (time of growth - 30 min). Methane concentration was varied by changing the flow rates in range of 0.3 to 0.8 l/h. Deposition temperature was varied by changing the distance between the substrate and the water-cooled holder in range of 600 to 900°C. To provide statistically averaged data the numerical analysis of shapes has been performed for 50-100 individual crystallites on each sample. In accordance with [2] the value of $\boldsymbol{\alpha}$ parameter can be evaluated from dimensions of diamond crystallites with use of formula shown in Fig. 1. The obtained dependencies of $\boldsymbol{\alpha}$ are shown in Fig. 2.

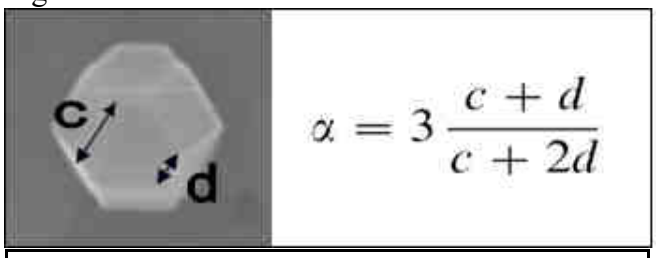

Figure 1. SEM image of a diamond crystallite on the silicon substrate and formula for calculation of parameter $\boldsymbol{\alpha}$.

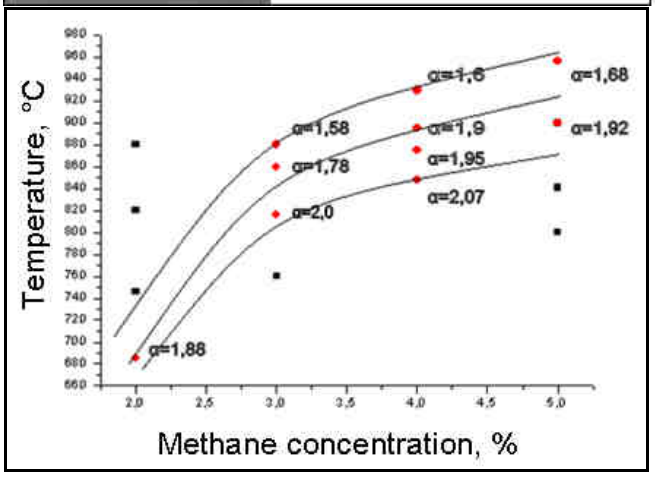

Figure 2. Diagram of dependence of $\boldsymbol{\alpha}$ *on the substrate temperature and the methane concentration in the gas mixture.*

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GRAPHITIZATION OF DIAMOND MICROCRYSTALS

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The diamond materials are known by various unique physical properties, which can be used for different practical applications. Recently mass production of diamond single crystals with perfect pyramidal shapes with use of chemical vapor deposition method and selective oxidation has been developed [1]. The micron-sized diamond tips produced by this method have shown excellent performance in use as probes in atomic force microscopy [2]. Such kind of tips has several advantages comparing to ordinary silicon probes. By having perfect crystal ordering and shape with a small size of apex these pyramids are convenient for investigation of diamond structure transformation into graphite. This transformation is important for application to provide conductive probes for tunnel scanning microscopy.

In this work we investigate graphitization of the pyramid shaped diamond microcrystals in course of thermal annealing in different gas environments (air, argon, nitrogen). The topology and surface structure modifications of the diamond tips were investigated with use of scanning electron microsopy and Raman spectroscopy. The annealing has been performed in a tube oven with constant gas flow at temperatures in range of 400 to 1200°C. We found that heating in oxygen contaminated atmosphere leads to oxidation of the film material with rates depending on its structural perfection (the smallest fractions are oxidized faster; the graphite type fractions are oxidized faster in comparison with diamond). Sample heating in oxygen free atmosphere did not change phase composition and film morphology for temperatures lower than 700°C. With higher temperatures we observe graphitization of diamond. The relative amount of graphite phase was estimated from Raman spectra. We propose an empirical model describing graphitization process.

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SENSORS BASED ON FUNCTIONALIZED SINGLE WALLED CARBON NANOBUD NETWORKS

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Recently, different types of CNT-based sensors have attracted tremendous attention. They can be made sensitive, ultra compact and with low power consumption. Additionally low fabrication cost can be reached when usages of CNT networks [1]. However, CNT based sensors have low selectivity. Functionalization of CNT is needed to reach the necessary selectivity and sensitivity. Functionalization of CNTs is a challenge due to their chemical inertness. Carbon nanobud (CNB) is a novel nanoscale hybrid material consisting of fullerenes, covalently attached to the outer surface of CNT [2]. CNBs have much higher chemical reactivity in comparison to CNTs and allow the charge transfer between fullerenes and nanotubes. These properties make CNBs promising sensor material. In this work we present experimental results of a systematic study of light and gas sensors based on functionalized CNB networks.

Tetrapyrydilporphyrine was utilized as a photo active dye and Nile Blue was chosen as an alcohol sensing molecule. Bingel reaction or a mild oxidation treatment was used for chemical attachment of sensing molecules to the CNB surface. Two principles are used in sensors: measurement of film resistivity and drain current of field-effect transistors (FET) built on functionalized CNB networks. Reversible changes in resistivity and FET drain current are found when the devices are exposed to light or alcohol vapor. The ethanol sensors have a sensitivity with linear dependence on ethanol concentration (~1 $\Delta R/R$, % on mol.%) and minute scale response rate.

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SIZE-INDUCED EFFECTS IN CRYSTALS OF GALLIUM SELENIDE

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Gallium selenide crystals are widely used as an active medium in semiconductor lasers. With the crystal size reduction beyond a threshold value, their properties, including the band gap value, starts to vary. This results into the shift of photoluminescence band positions. Due to this the photoluminescence can be observed within a certain spectral range.

In the work the results of investigation of such size effects are described [1]. GaSe nanoparticles could be formed in the reaction of an organometallics (GaMe3) with a trioctyl phosphine selenium in a high temperature solution of a trioctyl phosphine and a trioctyl phosphine oxide. A size of nanoparticles, obtained by this method, reached 2-6 nm. The corresponding photoluminescence bands were positioned at 360-450nm. As a result, the photoluminescence bands were shifted toward UV region, respectively to those of the bulk crystals [2, 3].

To obtain nanocrystals we used in this work a method of ultrasonication in an aqueous solutions of surfactant (pluronic F127), followed by a micro-filtration.

To estimate the size of GaSe nanoparticles, the spectra of optical absorption have been measured. For the large GaSe crystals the absorption shoulder is situated at 630 nm (at room temperature). It moved toward the UV region after the ultrasonication treatment followed by the micro-filtration. This blue shift is considered as an indication of a presence of nanoscale particle.

This work was supported by RFBR-09-02-91231, RAS programs and federal target program "Scientific and pedagogic personnel of innovative Russia" 2009-2013.

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SORTING CARBON NANOTUBES BY DENSITY GRADIENT ULTRACENTRIFUGATION

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Single-wall carbon nanotube (SWNT) is a rolled graphene sheet with a diameter of approximately 1 nm. SWNTs exhibit metallic or semiconducting properties, depending on how graphene sheets are rolled up. SWNTs have attracted a great interest in various applications. They are especially promising for nanoelectronic devices since their properties greatly depend on their geometrical parameters and electronic structures.[1] However, as-produced SWNTs always contain both metallic and semiconducting SWNTs, and that is a crucial problem towards applying them. Separation techniques can provide extraction of fixed nanotubes from any synthesized diameter distribution.

Nowadays there is a number of methods of SWNTs separation. Density-gradient ultracentrifugation (DGU) is the most suitable technique to obtain metallic or semiconducting SWNTs regardless of their production techniques and average diameters.[2,3] The method represents separation of individual surfactant-encapsulated SWNTs by diameter or electronic type via distinction in density determined by the tubes' diameters. The result, however, greatly depends on SWNTs synthesis technique, type and concentration of the surfactants, accuracy of the gradient preparation.

In this work high purity metallic and semiconducting SWNTs have been obtained by DGU technique (colored fractions in the picture). Influence of DGU parameters (type and concentration of the surfactants, accuracy of the gradient preparation) has been studied. Their optimization has resulted in extraction of metallic and semiconducting SWNTs fractions containing nanotubes with a narrow (less than 0.1 nm) diameter distribution. Obtained liquid fractions and films have been investigated by UV-VIS-NIR optical absorption spectroscopy and photoluminescence.

Thanks for support in frames of RFBR-10-02-00792 and RFBR-09-02-01051 projects

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Wednesday, August 4

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Harvesting Waste Thermal Energy Using a Carbon-Nanotube-Based Thermal-Electrochemical Cell

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Low efficiencies and costly electrode materials have limited harvesting of thermal energy as electrical energy using thermo-electrochemical cells (or 'thermocells'). We demonstrate thermocells, in practical configurations (from coin cells to cells that can be wrapped around exhaust pipes), that harvest low-grade thermal energy using relatively inexpensive multiwalled carbon nanotube (MWNT) electrodes. These electrodes provide high electrochemically accessible surface areas and fast redox-mediated electron transfer, which significantly enhances thermocell current generation capacity and overall efficiency. Thermocell efficiency is further improved by directly synthesizing MWNTs as vertical forests that reduce electrical and thermal resistance at electrode/substrate junctions. The efficiency of thermocells with MWNT electrodes is shown to be as high as 1.4% of Carnot efficiency, which is 3-fold higher than for previously demonstrated thermocells. With the cost of MWNTs decreasing, MWNT-based thermocells may become commercially viable for harvesting low-grade thermal energy.

THERMAL PROPERTIES OF GRAPHENE AND OTHER LOW-DIMENSIONAL CARBON MATERIALS

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We have discovered that suspended graphene, in addition to its unique electronic and optical properties, reveals unusually high thermal conductivity exceeding that of diamond or carbon nanotubes at room temperature [1-2]. The measurements were carried out using an original non-contact optical technique on the basis of micro-Raman spectroscopy. The fact that the phonon thermal conductivity of large enough graphene sheets should be higher than that of basal planes of bulk graphite was predicted theoretically by Klemens [3] a decade ago. He pointed out at a fundamental difference in the low-energy phonon transport in the two-dimensional (2-D) graphene and 3-D graphite. In this talk we review our experimental results for the single-layer graphene (SLG) and few-layer graphene (FLG), and describe theoretically how the thermal conductivity of graphene sheets depend on their width [4-5] and the number of atomic planes as one goes from graphene to graphite. We specifically consider the three-phonon Umklapp scattering in SLG and bi-layer graphene (BLG), and show that in SLG the phonon Umklapp scattering is quenched leading to the conditions when heat transport is only limited by the in-plane edge boundary scattering. We compare the heat conduction properties of graphene and FLG with those of other nanocarbon materials [6-7]. The obtained results are important for the proposed applications of graphene and FLG in electronic and optoelectronic devices, and in thermal management [8].

The work at UCR was supported, in part, by DARPA – SRC Center on Functional Engineered Nano Architectonics (FENA) and Interconnect Focus Center (IFC).

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OPTICAL AND OPTOELECTRONIC PROPERTIES OF GRAPHENE

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Graphene is a single atomic layer (or a few layers) of carbon atoms arranged on a two-dimensional hexagonal honeycomb structure. Although graphene was discovered experimentally just 6 years ago [1] the material has attracted great attention especially due to its significant electrical and mechanical properties. The optical properties of graphene are as well fascinating. An atomic layer thick material absorbs photons between the visible and infrared wavelengths, and the interband transition strength is one of the largest among all materials. Optical microscopy is the most important method to locate and identify graphene on a substrate, often in combination with Raman spectroscopy. The contrast between graphene and the substrate is the crucial factor for optical graphene identification. Interestingly the transparency of graphene depends only on the fundamental property, the fine structure constant. Nevertheless, many new optical and optoelectronics applications of graphene have been reported. This review will discuss the optical properties and (opto)electronic applications of graphene.

One of the most promising optical applications of graphene is probably its use as a transparent conducting film e.g. for flexible electronics and solar cells. High conductivity, transparency and stability may facilitate graphene to challenge the existing ITO based films. However, the lack of good fabrication method has limited the size and material quality of graphene needed for practical electronic and photonic devices. A very recent work on chemical vapour deposition (CVD) synthesis of ultra-large area monolayer graphene films and roll-based layer-by-layer transfer onto flexible substrates demonstrated excellent large-area film quality [2]. Ultrafast photodetectors made from single- and few-layer graphene have been demonstrated [3]. The devices showed high bandwidth, very wide wavelength detection range, zero dark current operation, good internal quantum efficiency and ease of fabrication. In spite of being zero bandgap semiconductor graphene also shows wavelength-independent saturable absorption [4]. Thus it is possible to use graphene to make a wideband saturable absorber for laser mode locking.

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BAND GAPS IN SINGLE WALL CARBON AND BORON NITRIDE NANOTUBES

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The band gaps of semiconducting single wall carbon nanotubes are known to depend on their diameter and helicity. First experimental evidence was provided by pioneering scanning tunneling microscopy and spectroscopy (STM/STS) experiments [1]. In these experiments, diameter dependence was analysed within the framework of a tight binding mode, which neglects many-body effects. However, in 2005, optical luminescence measurements have revealed the importance of these effects, by demonstrating the existence of huge excitonic effects, with an exciton binding energy equal to about 1/3 of the band gap [2]. In order to solve this controversy, we have performed extensive STS investigation of carbon nanotubes using a low temperature STM operating under UHV conditions and by coupling the measurements with TEM analyses of the structure and optical absorption measurements [3]. STS measurements of electric arc carbon nanotubes, which display a narrow diameter distribution and are most assembled into bundles, have revealed a screening effect due to gold substrate which results in a gap reduction, depending on the tube-substrate distance. In an oversimplified scheme, by describing the screening term as inversely proportional to the tube-surface distance, we have determined the intrinsic gap of the tube from STS measurements. Furthermore, we have compared STS results with optical absorption measurements on the same sample. The difference in energy found between optical transition and STS intrinsic gap related to semi-conducting tubes provides a value of the exciton binding energy, fully compatible with luminescence experiments [3]. These results provide a deeper knowledge of many-body interactions in these 1D systems and solve the apparent controversy between the pioneering STM measurements, and optical experiments [1, 2].

Furthermore, STS allows us also to image directly the wave functions at the Van Hove singularities of the semiconducting and metallic single wall nanotubes. Local conductance measurements show spectacular carbon-carbon bond asymmetry at the Van Hove singularities for both semiconducting and metallic tubes, demonstrating the symmetry breaking of molecular orbitals in nanotubes. Whatever the tube, only two types of complementary orbitals are alternatively observed. We show, by extending earlier arguments [4], that the observed conductance images, including spectacular complementary effects when going from one singularity to the other, can be accounted

for very accurately, using the simplest tight-binding model, confirmed by ab initio calculations [5].

Boron nitride nanotubes are the analogue of carbon nanotubes, being composed of rolled up hexagonal boron nitride (h-BN) sheets. Due to the ionic character of the BN bond, they are expected to have very different optical properties, with gaps in the far UV range, about 6 eV. Strong excitonic effects have also been predicted theoretically, and have been recently observed in h-BN as well as in multiwall nanotubes [6,7]. Combinations of cathodoluminescence, photoluminescence and excitation spectroscopies have provided us with a good semiquantitative description of the optical properties of these systems, which will be reviewed. Preliminary results of micro photoluminescence on single wall BN nanotubes will also be presented.

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Thursday, August 5

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FORMATION AND PROPERTIES OF ONION-LIKE CARBON

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Carbon is the only element providing the formation of different families of nanostructures - fullerenes and onion-like carbons, single- and multi-walled nanotubes, carbon fibers, aerogels and foams, nanodiamonds, and recently derived nanographene species. Carbon-based materials play an important role in production of electromagnetic (EM) absorbing and EM shielding composites because of their lightness and suitable electronic properties. It was demonstrated that using nanostructured elements assembled at different length scale within the binding matrix could result in tunable dielectric response over a wide frequency range. Here we consider EM response properties of a recently discovered form of nanocarbon – onion-like carbon (OLC) in a wide range of EMI (from radio frequencies up to UV).

We have found that OLC is formed during the annealing of explosive nanodiamond of size 2-10 nm (ND). Controllable graphitization in vacuum or argon of the explosive nanodiamond within the temperature range 1200-1900 K allows producing the diamond/nanographite composites with variable ratio of decreasing in size diamond core and defective curved graphitic shells (sp^2/sp^3 nanocomposites). As annealing temperature is increased the ratio between diamond core and outer defective curved graphitic shells (sp2/sp3 nanocomposites) decreases, finally resulting in OLC structure. Due to the aggregation of primary ND its annealing products (OLC particles) are organized into aggregates with joint defective graphene shells covering several primary OLC cores. Small size of curved graphitic shells, the presence of interface between nanosize diamond cores and graphitic shells and probably high concentration of open graphitic edges can cause the unusual electrophysical properties of OLC and OLC based composites. Thus OLC possesses a unique structure consist of agglomerates of concentric fullerene-like spheres, satisfying the criterion of hierarchical assembly with tunable electrophysical properties.

All these materials are under intensive studies. They were characterized with HRTEM, Raman spectroscopy, XRD, XPS, EELS, ESR, X-ray emission spectroscopy and the electrical resistivity measurements. EM response of different types of OLC was investigated in a wide range of EMI (from radio frequencies up to UV). It was demonstrated that OLC is a perspective material for electrochemical applications and attenuation of electromagnetic irradiation. Due to a very efficient optical limiting action of OLC it is good candidates towards photonic applications. Possible mechanisms of EM response in a wide frequency range of OLC based systems are discussed.

NOISE IN NANOCARBON DEVICES AT MICROWAVE FREQUENCIES

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Measurement of non-equilibrium current fluctuations provides invaluable information to supplement the regular conductivity measurements in nanoscale samples. We have employed this technique to investigate transport both in nanotubes and graphene at cryogenic temperatures down to 50 mK. We have identified several different transport regimes: ballistic [1], diffusive [2] and pseudodiffusive [3]. Ballistic behavior is found in single walled carbon nanotubes with Fabry-Perot interference patterns, while diffusive transport is prevalent in multiwalled tubes. Ballistic graphene at the Dirac point, however, emulates diffusive behavior because the transmission eigenvalues of the available evanescent modes form a set equivalent to that in a diffusive wire. We have verified that the transmission eigenvalues vary as a function of the carrier density and geometry, and that pseudo-diffusive behavior is only seen when the width-to-length ratio W/L > 3. In my talk, I will discuss our experimental findings on these issues and briefly mention how superconducting contacts change the situation.

We have also investigated electrometers based on nanocarbons. In order to achieve ultimate charge sensitivity at large band width, carbon nanotube rf-SETs [4, 5] or CNT-FETs [6, 7] are both excellent choices. These devices are rivalled by CNT Josephson junction electrometers, which are, in principle, dissipationless, and therefore possess only a small back action noise. Superconducting graphene devices we have employed as flux detectors with excellent sensitivity. I will review the principles of these devices and present the record sensitivities achieved in our experiments. This work was supported by the Academy of Finland and by the EU contract FP6-IST-021285-2 (www.CARDEQ.eu).

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AEROSOL SYNTHESIS AND MECHANISM OF SINGLE-WALLED CARBON NANOTUBE FORMATION

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One of the most important issues in the understanding of the mechanism of the CNT growth is the role of the catalyst particles. In this paper we attempted to answer the questions concerning the active catalyst phase resulting in the formation of SWCNTs. Can oxide be a catalyst? Can carbide catalyze the synthesis of CNTs? What is the temperature dependence of the growth rate of SWCNT? Also we investigated another important issue recently raised by Yao *et al.* [1], whether the diameter and therefore chirality of SWCNTs can be tuned during the SWCNT growth by changing the temperature during the synthesis process.

Here, we report the investigations of the formation mechanism of single-walled carbon nanotubes (CNTs) by two different aerosol (catalyst floating) methods. In the first method, Fe catalyst particles were produced using a hot wire generator (HWG) [2]. The second method is based on the ferrocene vapor decomposition in carbon monoxide atmosphere [3]. In order to investigate the processes occurring in the reactor we have carried out *in situ* sampling from different locations in the reactor. Catalyst particles captured before SWCNT nucleation as well as inactive particles were determined to have cementite (Fe_3C) phase, while particles with γ- and α-Fe phases were found to be embedded in the SCWNTs. The growth rate in the temperature range from 804 to 915 °C was respectively varied from 0.67 to 2.7 μm/s. The growth rate constant can be described by an Arrhenius dependence with an activation energy of E_a = 1.39 eV, which was attributed to the carbon diffusion in solid iron particles. CNT growth termination was explained by solid-liquid phase transition in the catalyst particles. A high temperature gradient in the reactor was found to not have any effect on the diameter during the SWCNT growth and as a result on the chirality of the growing SWCNTs. [4] On the basis of parametric investigations and *in situ* sampling experiments the mechanisms of CNT formation are proposed.

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CVD DIAMOND: GROWTH AND CHARACTERIZATION

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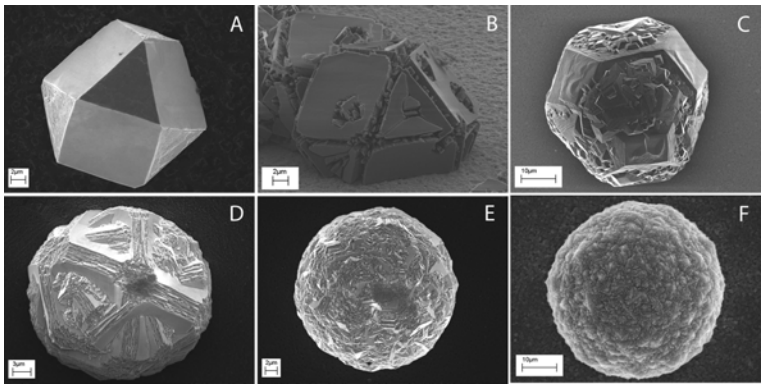
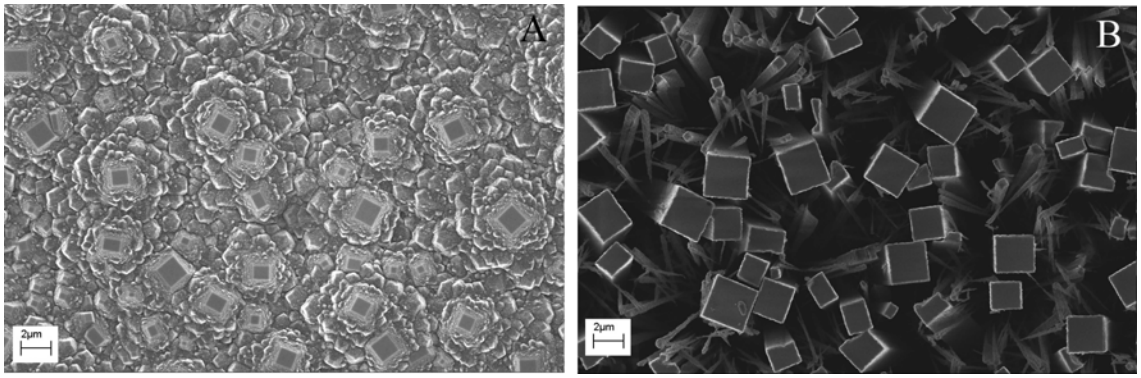
Diamond films and individual crystallites were obtained by DC PECVD with different methane concentrations. Correlation of CVD process parameters with structure and composition of the films via using various experimental techniques (optical emission spectroscopy, Raman spectroscopy and scanning electron microscopy (SEM) was investigated.



SEM images of CVD diamond crystallites grown at different methane concentrations

0.5% (A)
1% (B)
2%(C)
3%(D)
4%(E)
6%(F)

A thermal oxidation process of diamond films has been studied. The oxidation was realized via heating of the CVD films in air. Pristine and oxidized CVD diamond films were analyzed with Raman spectroscopy and SEM techniques. Raman spectroscopy revealed substantial changes in the polycrystalline diamond film composition induced by oxidation. A selective oxidation of disordered carbon and small size diamond crystallites was obtained at appropriate temperatures. A model explaining the formation and oxidation of the CVD diamond films containing the micrometer single diamond cores surrounded by the nanocrystalline diamond and disordered carbon has been proposed on the basis of the obtained results.



SEM images of CVD diamond film: (A) before and (B) after thermal oxidation

SELECTIVE GROWTH OF HIGH QUALITY SWNTS WITH MONOMETALLIC CATALYST

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Small diameter single-walled carbon nanotubes (SWNTs) are regarded as potential building blocks in nanoelectronics. Obtaining (SWNTs) with narrow (n,m) chirality distribution are highly desirable since the electronic properties of SWNTs strongly depend on their diameter and chirality.

Herein, we report the growth of small diameter SWNTs from nickle-contained catalysts deposited on silica support by atomic layer deposition (ALD) technique. Various techniques were employed to analyze both the catalysts and SWNTs: Temperature Programmed Reduction (TPR), Raman, Absorption and Fluorescence Spectroscopy, Scanning electron microscope (SEM), ultra-high resolution transmission electron microscope ((Jeol JEM-2200FS double Cs corrector TEM).

Raman spectra have convinced that SWNTs have been successfully grown by thermal CVD at 450 °C. High quality SWNTs can be grown at 500 °C or above, as proved by Raman spectra (I_G/ I_D =28). SWNTs diameters mainly range from 0.7 nm to 0.9 nm. UV-vis-NIR spectra and photoluminescence spectra verify that the produced nanotubes have only a few species. Decreasing the reaction temperature leads to a progressive narrowing of the diameter distribution, this result is coincided with Raman spectra, photoluminescence intensity maps. Meanwhile, the mechanism for successful growth of SWNTs at low temperature by monometallic catalyst has been provided.

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GROWTH AND CHARACTERIZATION OF ULTRANANOCRYSTALLINE DIAMOND FILMS

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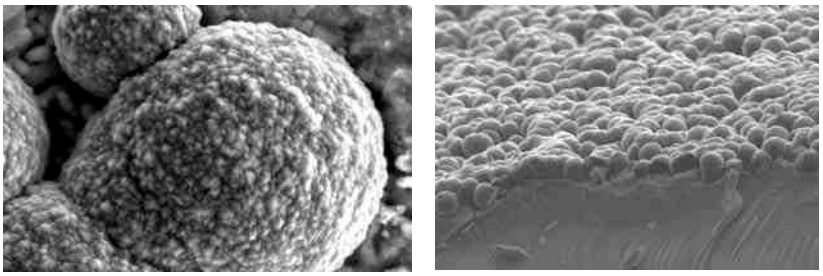
Specific properties of ultrananocrystalline diamond (UNCD) films (i.e. diamond material with grain sizes less than 10 nm) suggest significant potential for applications in such fields as MEMS/NEMS, electrochemistry, biology [1] and photonics [2]. Characterization of UNCD films is still not complete in many aspects including its structural peculiarities and growth mechanisms.

In this work UNCD films were obtained by chemical vapor deposition (CVD) method and characterized by Raman spectroscopy (RS), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). This comprehensive study, together with data on the influence of growth parameters on film's morphology, made us capable to reveal the inner structure, the phase composition and to suggest a model, describing possible mechanism of UNCD film formation. Examples of SEM images and Raman spectrum of UNCD film are represented on Fig.1(a, b) and Fig.2 respectively.



(a) (b)

Fig.1. SEM image of UNCD film, magnification 50 000x (a) and 10 000x (b)

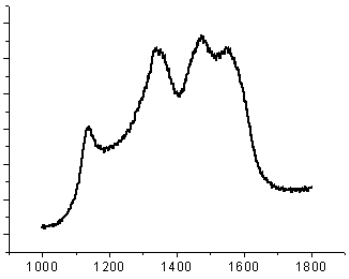


Fig 2. Raman spectrum of UNCD film

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POST-GROWTH ALIGNEMENT OF SINGLE-WALL CARBON NANOTUBES THROUGH SELF-ASSEMBLY

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Carbon nanotubes can be considered as anisotropic objects due to their high aspect ratio. Their electrical and optical properties (conductivity, optical absorption etc.) depend strongly on the nanotube orientation. The random orientation of nanotubes is the main obstacle that inhibits a possibility to observe the anisotropy on a macroscopic scale (in liquids or on substrate).

To align nanotubes several post-growth methods have been proposed. To a certain extent, the alignment can be achieved by means of mechanical stretching of the nanotube films [1, 2]. However in this case the alignment process is limited by the maximal elongation of the film containing the nanotubes. The second approach [3] uses the Lagmuir-Blodgett technique. As a result, the horizontally aligned nanotubes can be deposited on the substrate. The layer of closely packed highly ordered nanotubes has a one-molecule thickness. A promising method has been realised in paper [4]. The authors have dealt with a self-assembly process of nanotubes. It may take place in liquid suspensions. Nanotubes tend to be oriented in parallel in liquid, behaving as a nematic liquid crystal. In case of vertical insertion of a smooth substrate into the nanotube suspension, during liquid evaporation, the nanotubes align in a horizontal direction on the substrate.

This method has been realized in the present work. A glass substrate was deepen vertically in the aqueous suspension of single-wall carbon nanotubes (SWNT). The vial with the SWNT suspension stayed on the anti-vibration table while the liquid was evaporating. After the drying process (which took about 5 days) the ordered structures of horizontally aligned nanotubes were observed.

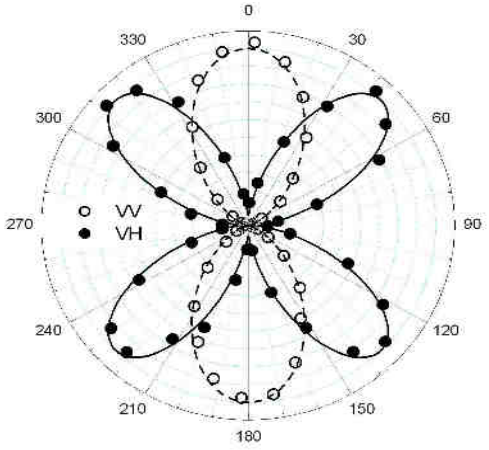

Fig.1. Intensity of Raman line 1592 cm^{-1} depending on the angle between the incident light polarization and the nanotube axis.

The polarized Raman studies have revealed a narrow angular distribution of nanotube orientation. The profiles of the signal intensity vs. the orientation of nanotube relatively to the direction of the laser polarisation are presented on the Fig.1. Supposing that the angular distribution of nanotubes on the substrate is gaussian, the halfwidth of the distribution can be derived. In present case it is less than 7 degrees.

This work was supported by RFBR-10-02-00792 and 09-02-91076, and RAS programs.

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OPTICAL ABSORPTION AND RAMAN SPECTROSCOPY INVESTIGATION OF GRAPHITE FLUORIDES

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Graphite fluorides are layered two-dimensional materials, which have been systematically studied in 70-80 years of the last century [1]. Depending on synthesis method graphite fluorides CF_x ($x \leq 1$) with different composition can be obtained. In the stoichiometric compounds, CF and C_2F, fluorine atoms form covalent bonds with each carbon atom or with half of carbon atoms of a graphene layer. The large interlayer spacing (more than 0.6 nm) allows preparing intercalates with various molecules. Graphite fluoride C_2F attracts much attention due to preserving of π-electrons. There are high-temperature and low-temperature methods for synthesis of C_2F and fluorine pattern is probably will be dependent on the synthetic conditions. In this contribution we present results on the investigation of poly(dicarbon monofluoride) $(C_2F)_n$ prepared in mild conditions using BrF_3 as a fluorinating agent at room temperature [2]. A study of this compound by X-ray emission and X-ray absorption spectroscopy revealed that the most probable structure of $(C_2F)_n$ is alternation of fluorocarbon and bare carbon chains [3]. Different units of π-electron system, such as double bonds, hexagons, one-dimensional chains, and delocalized electron areas, will be manifested in optical absorption spectra and Raman spectra at different energy. Investigation of graphite fluorides intercalated with C_6H_6, CCl_4, CH_3CN showed two additional features around 1504 and 1425 cm^{-1} located between the D and G modes characteristic of graphite materials. Irradiation of $(C_2F)_n$ with high energetic particles was found to result in lowering of relative intensity of the former band that by results of X-ray photoelectron spectroscopy was related to detachment of fluorine atoms. Graphite fluorides are optically transparent compounds which color can change from slightly yellow to blue. Optical absorption spectra of the investigated compounds revealed a set of bands in the range from 0.5 to 5 eV, which was attributed to transitions of π-electrons.

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INFLUENCE OF STRUCTURAL CHARACTERISTICS OF ALIGNED CARBON NANOTUBE FILMS ON THE DIRECTION OF X-RAY SCATTERING

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Interaction between X-ray radiation and carbon materials is extremely important for design of novel X-ray optical elements. Carbon nanotubes (CNT), according to their cylindrical structure and small cross-section, have specific features in interaction with an X-ray radiation. Measurements of angular dependence of X-ray fluorescence of multiwall CNT films, oriented perpendicularly to the substrate surface, are represented in this work. We show that structural characteristics of multiwall CNTs film influence the form of X-ray scattering curve. Optical scheme of experiment is presented in Fig 1(a). Comparison of X-ray scattering curves for the initial and mechanically disoriented CNT samples indicated increasing of X-ray fluorescence intensity by ~3 % in the direction of CNT grow. Information about orientation of nanotubes in a film can be obtained from X-ray scattering curves measured for aligned CNTs and those after alignment breakage. Comparison between experimental curves of X-ray fluorescence scattering and theoretical curves, calculated in framework of the radiation absorption approximation, indicated that coefficients of genuine absorption for aligned and disordered CNTs are different. The influence of surface film layer consisting of disordered CNTs on the form of X-ray scattering curve is shown. Increasing of escaped intensity of X-ray radiation was detected when surface contaminations were removed by electro-mechanical treatment (Fig. 1(b)). Possibility of X-ray fluorescence propagation alone the nanotubes constituting a film is discussed. It was suggested, that the main reason of orientational influence of CNTs on C Kα-radiation propagation is the fulfilment of the conditions of anomalous dispersion and total internal reflection.

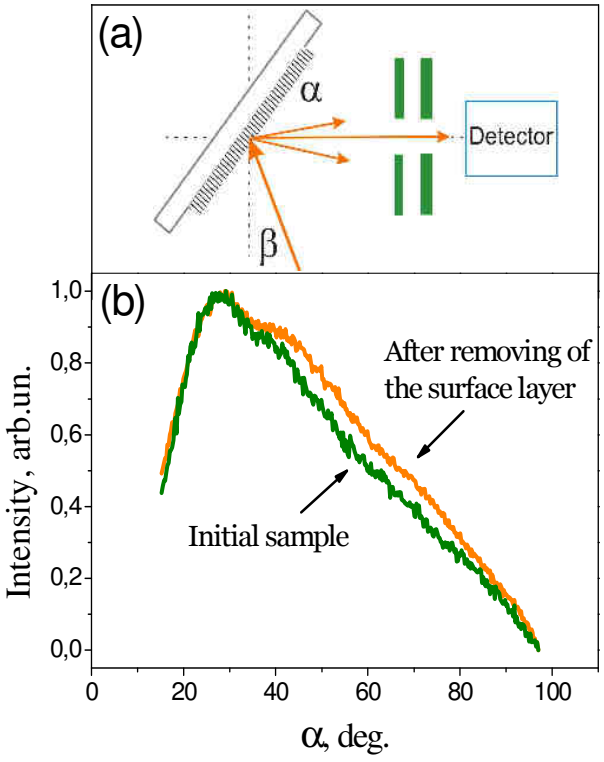

Fig.1. (a) Optical scheme of experiment; (b) X-ray scattering curves of initial sample and after removing of the surface contamination.

VIBRATIONAL SPECTRA OF TRIFLUORMETHYLFULLERENE DOUBLE CAGE CYCLOADDUCTS

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Novel substances comprising two and more fullerene C_{60} cages covered by trifluormethyl addends were discovered by means of MALDI mass-spectrometry (Brucker Autoflex II, N_2 laser, DCTB as a matrix) among products of trifluormethylation of sodium fullerides Na_xC_{60}, x = 1, 3, 6, 10. The content of these compounds didn't exceed 1 – 2wt% of total trifluoromethylfullerenes amount. According to mass-spectra, a set of compounds with general formula $(C_{60})_n(CF_2)_m(CF_3)_kF_x$ where n=2, 3, m=2, 4, 6, k=24-32 was formed. Post source decay spectra evidence detachment of only CF_3 and F addends while no CF_2-group's loss was registered. Thus the formation of CF_2 junctions between two carbon cages is thought to be preferable. Two CF_2-groups and four cage carbon atoms of adjacent carbon skeletons form a six-membered cycle connecting fullerene spheres. Experimental *IR* spectrum (Tensor 27, Bruker) of Na_3C_{60} trifluormehylation product contains several strong wide bands pointing on presence of CF_3 groups and fullerene cage, as well as one additional band at 1124 cm^{-1} which was not observed earlier for trifluormethylfullerenes. Quantum chemical calculations at DFT level of theory (Priroda software package [1], PBE exchange-correlation functional and basis set of triple zeta quality) were performed to evaluate the *IR* frequencies of CF_2-bridge vibrations of a model molecule $C_{60}(CF_2)_2C_{60}$ with a six-membered carbon cycle connecting fullerene units. Previously a scale factor was found from comparison of calculated and experimental *IR* spectra of individual trifluormethylfullerene S_6-$C_{60}(CF_3)_{12}$ [2], obtained by the synthetic procedure similar to utilized in this work. Application of this scale factor leads to a good convergence of theoretical and experimental spectra of Na_3C_{60} trifluormethylation product. The band at 1124 cm^{-1} was found to correspond to oscillations of CF_2-bridge groups. Thus, the *IR* spectrum is in accordance with the hypothesis of six-membered junction between fullerene spheres in multi-sphere derivatives identified in this work.

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IN-SITU PECVD DIAGNOSTIC BY OPTICAL EMISSION SPECTROSCOPY CHARACHTERIZATION OF GAS DISCHARGE PLASMA

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Carbon nanotubes (CNT) due to their unique properties have been identified as a potentially useful material for a wide range of applications in nanoscale devices and technologies. The most usual way to produce CNT is chemical vapor deposition (CVD) from gas mixtures containing carbonaceous components activated in gas discharge plasmas of different types. In order to fully exploit CNT, better understanding of the CVD processes is essential. In particular, identification of the primary growth species and their spatial distribution in the gas environment is necessary for understanding CNT growth mechanism and for optimization of the CVD process parameters. One of the most convenient and informative non-intrusive technique is optical emission spectroscopy (OES).

We report on characterization of direct current discharge plasma-enhanced chemical vapor deposition of CNT films in a hydrogen-methane gas mixture. The optical emission spectra were obtained for 6,5% methane concentrations at total pressure 70 Torr. The measurements were taken in the range of 250 – 750 nm wavelengths (Fig. 1). The structure of carbon thin-film materials were characterized qualitatively by Raman spectroscopy and electron microscopy.

The data obtained by optical emission spectroscopy show presence of H, H_2 and C_2 activated species in the discharge plasma. The spectral measurements were made in different areas of the plasma. Spatial distribution of the most intense C_2 emission line at 516,5 nm in the Swan system ($d^3\Pi_g$-$a^3\Pi_u$) of DC-discharge have been studied.

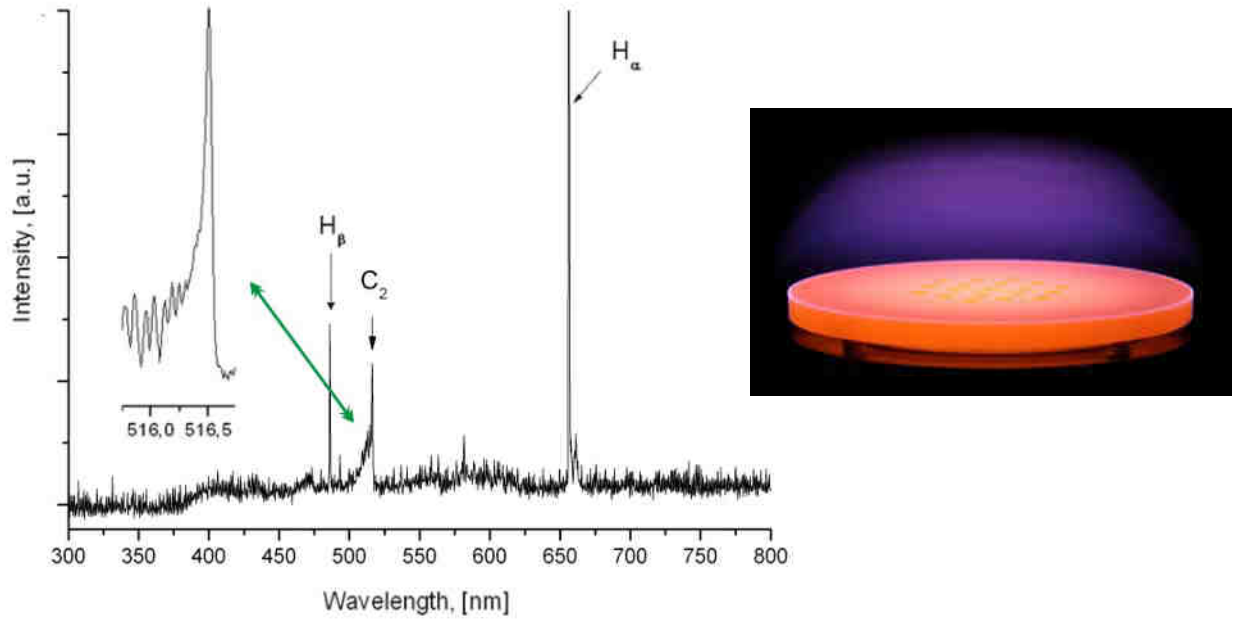

Figure 1. Typical emission spectra for hydrogen-methane gas mixture and photograph of the plasma above Nb anode plate

RAMAN PROBING OF UNIAXIAL STRAIN IN INDIVIDUAL SINGLE-WALL CARBON NANOTUBES IN A COMPOSITE MATERIAL

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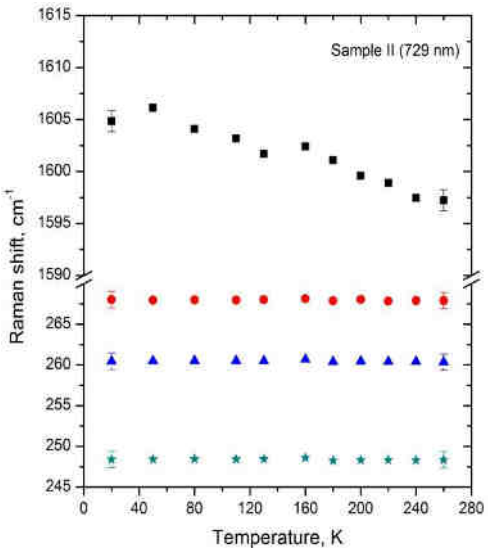
Environmental effects on the optical properties of single-wall carbon nanotubes in a gelatin-based composite material were studied by Raman spectroscopy and Photoluminescence.

Then temperature measurements in the range 20-290 K on different samples were made. In figure 1, typical temperature dependencies of the frequency of the RBM and that of the most intense G-mode are displayed. Similar behavior of Raman-active modes was found at other excitation wavelengths. Namely, frequencies of G-band tangential modes shifted downward with increasing the temperature (for about 10-20 cm^{-1}), while radial breathing modes frequencies almost did not change in the whole temperature range.

These behaviors contrast to temperature dependence of the Raman modes of SWCNTs measured in the same temperature range [1]. The observed behavior suggests tensile deformation of SWCNT in SWCNT@gelatin induced by temperature. The deformation is due to the difference between the dilatation coefficients of the tubes and gelatin respectively. According to recent ab initio calculations [2] the frequencies of the low-frequency Raman-active modes almost do not change, while the high-frequency G bands shifts linearly under uniaxial strains.



This study brings evidence for the extreme sensitivity of nanotubes to their environment. The strain induced spectral shifts in Raman and Photoluminescence spectra reveal important information about the mechanical properties of such composite material and their relationship with the band structure of the nanotubes. Furthermore it provides evidence for an efficient load transfer from the matrix to the tube, which is of outmost importance for mechanical reinforcement applications.

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Small shell number multi-wall carbon nanotubes characterization by Raman spectroscopy

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Since carbon nanotubes opening, basic researches have revealed new possibilities of Raman spectroscopy for diagnostics of carbon nanostructures, about their conductivity type, nanotubes geometry, features of electronic levels structure. However in case multi-wall carbon nanotubes (MWNTs) Raman method is not such sensitive tool and there is opened a question on possibilities of a method for diagnostics of MWNT.

The Raman features associated the RBM from large diameter tubes is usually too poor to be observable. The Raman signal of small diameter inner tubes sometimes can be observed when a good resonance condition can be received. We did not manage to register a signal in the field of RBM. The Raman spectra MWNTs have been registered in three spectral regions, corresponding to *D* (disorder-induced), *G* (graphite) and *2D* (two-phonon scattering)-bands. In this work the Raman spectroscopy has shown its sensitivity to the structure of MWNTs of small diameter, grown with a compositional catalyst and treated afterwards heated in flow of pure argon. We have characterized as produced MWNTs with different diameters (series 1) and two types of tubes with fixed mean diameters (~10 and 20 nm) heated in a flow of pure argon at various temperatures (2200, 2600, 2800C° - series 2).

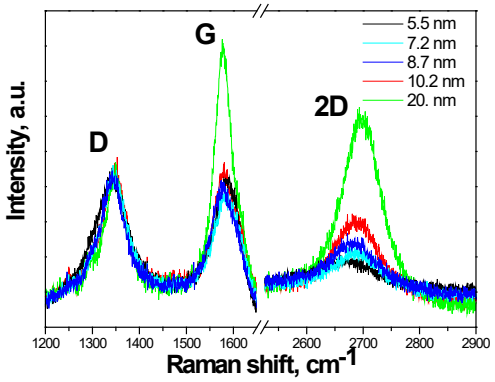

Figure 1 *Raman spectra of MWNT with diameters fixed by HRTEM images* ***(series 1)***.

A ratio of intensities I_{2D}/I_D for tubes of series 1 (Figure 1) has demonstrated almost a linear dependence on the nanotube diameter. After heating (series 2), *D* (disorder induced) Raman band has shown a substantial decrease in intensity. Variation of Raman spectra parameters are discussed in terms of defectiveness of nanotubes.

So, the Raman spectroscopy has shown its sensitivity to the structure of MWNTs of small diameter, grown with a compositional catalyst and treated afterwards with a vacuum heating.

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THREE-DIMENSIONAL RAMAN IMAGING OF DIAMOND NANOTIPS

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Diamond is a material known for its extreme mechanical and optical properties, thus of industrial importance as well as of scientific interest. The recent growth technique of chemical vapor deposition has made it possible to prepare high-quality diamond crystals in a form of films, needles [1], and nanotips [2].

We studied spatially resolved Raman spectra of diamond nanotips by using a confocal microscope system (Nanofinder30, Tokyo Instruments, Inc.). A laser beam at the wavelength of 532 nm was focused onto a single nanotip carefully mounted on a quartz plate (Figure 1a). By using a x100 objective, the spatial resolution of 275 nm is achieved. An intense Raman line was observed at 1332 cm^{-1} over the nanotip. The narrow linewidth, 2.8 cm^{-1}, indicates high crystallinity of the diamond. The three-dimensional Raman imaging of the nanotip was performed by scanning of the galvano mirrors. Figure 1b is an example of two-dimensional slices, which nicely show the triangular cross section of the conical nanotip. Interestingly, the Raman line shows broadening and a shift depending on the position in the sample. In the presentation, we will report the detailed analysis and discuss the origin of the broadening and the shift.

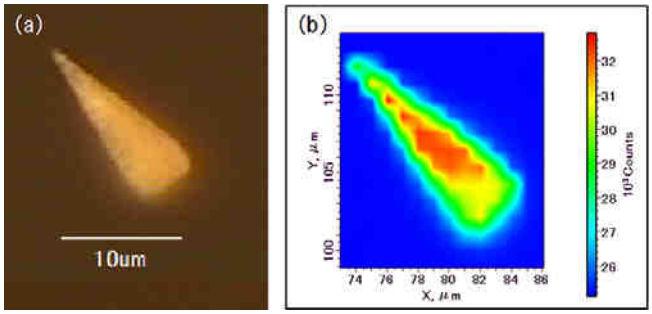

Figure 1 (a) Optical image of a diamond nanotip. (b) Two-dimensional mapping of the Raman line at 1332 cm^{-1} under 532 nm excitation of the same nanotip as in (a).

[1] A.N. Obraztsov, P.G. Kopylov, A.L. Chuvilin, N.V. Savenko, Diam. Rel. Mat. **18** (2009) 1289.
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ANALYSIS OF THE SIZE DISTRIBUTION OF SINGLE-WALLED CARBON NANOTUBES USING OPTICAL ABSORPTION SPECTROSCOPY

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The diameter of single-walled carbon nanotubes (SWNTs) is an important characteristic to determine their electronic properties and direct further applications in electronics and photonics. However, in all known fabrication methods, the as-synthesized SWNTs are produced in various diameters and chiral angles. A demand currently exists for an accurate and rapid method of evaluating the mean diameter and diameter distribution of bulk SWNTs.

In this work[1], the SWNT samples with various diameter distributions are synthesized by the gas-phase CVD approach. A novel method is developed for more efficient evaluation of the mean diameter and diameter distribution of a bulk SWNTs from optical absorption spectra. Without making a strict assumption on the form of the diameter distribution, the optical absorption from the transition energies of each nanotube is modelled by summing contributions over the entire absorption spectrum. The transition energies of a SWNT are described by a sum of Gaussian line shapes and known peak positions corresponding to the ETB/MB model (extended tight-binding model including many-body corrections). The highly ill-posed problem is well-resolved by the introduction of a regularization term in the fitting process. Verification of this protocol is based upon statistic analysis of hundreds of high-resolution TEM images as well as comparison with Raman measurements on the same SWNT samples. The very good agreement among different techniques indicates that this approach enables accurate and rapid assessment of diameter distribution and can be extended to bulk SWNTs with various diameter distributions.

[1] Y. Tian, H. Jiang, J.v. Pfaler, Zh. Zhu, A. G. Nasibulin, T. Nikitin, B. Aitchison, L. Khriachtchev, D. P. Brown and E. I. Kauppinen. J.Chem.Phys.Lett 1(2010) 1143.

Poster session II

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DIRECT SYNTESIS OF CARBON NANOFIBERS ON CEMENT PARTICLES IN FLUIDIZED BED REACTOR

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Carbon nanotubes (CNTs) and nanofibers (CNFs) are promising components for the next generation high performance structural and multi-functional composite materials. One of the largest obstacles to create strong, electrically or thermally conductive CNT/CNF composites is the difficulty of getting a good dispersion of the carbon nanomaterials in a matrix. Typically, time-consuming steps of the carbon nanomaterial purification and functionalization are required.

We propose a new approach to grow CNTs/CNFs directly on the surface of matrix and matrix precursor particles. As the precursor matrix we selected cement, the most important construction material. We synthesised a novel cement hybrid material, wherein carbon nanomaterials are attached to the cement particles in a fluidized bed reactors. The growth of this material was carried out in the aerosol form in a fliudized bed reactor. The synthesis conditions were optimised with a different ratio of acetylene, carbon monoxide and nitrogen in the temperature range of 550-650 ^{o}C. As a result, the carbon nanomaterial concentration achieved in the sample up to 30 %, which could be sucessfully utilized as a master bacth for the hardened paste and concrete production.

Our investigations based on TEM, SEM, XRD, TGA and Raman measurements showed high efficiency of the method for the low temperature and high yield synthesis of CNFs. Investigations of the physical properties of the cement hardened paste made of this material revealed as high as 2 times increase in the compressive strength and 40 times increase in the electrical conductivity after 28 days curing in water. The new synthesized material has been proven to increase 3 times the compressive strength of concrete.

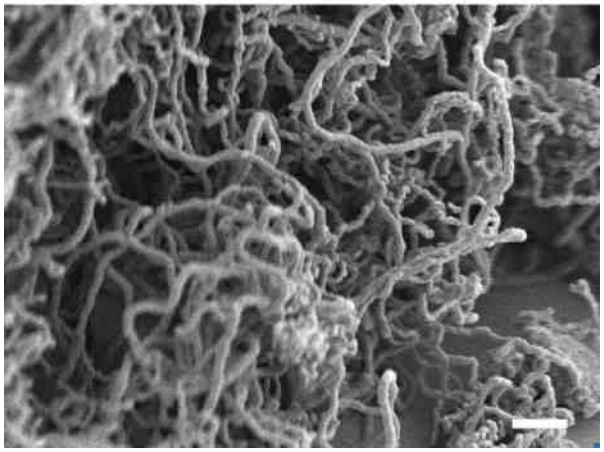

Figure. SEM image of cement particles covered by CNFs synthesised in a fluidized bed reactor at 550 ^{o}C in CO and C_2H_2 atmosphere (bar scale is 200 nm).

This work was supported by the Academy of Finland and by the Federal Agency for Science and Innovation of Russian Federation.

CHEMICAL VAPOR DEPOSITION FOR GRAPHENE FILM SYNTHESIS

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Graphene is one of the most interesting carbon nanomaterials. It is a two-dimensional hexagonal lattice of carbon atoms. A preparation of the large-area graphene samples is investigated during last five years. A chemical vapour deposition (CVD) from carbon-containing gas was used more than 20 years for growth of pyrolytic graphite on nickel. But only two years ago this method has been employed for growing a single graphene layer [1].

Here we present a simple and cheap hand-made CVD installation for graphene growing from a gas mixture of methane and hydrogen. The nickel and copper foils of different thickness (from 25 to 100 μm) were used as a substrate for deposition of the graphene film. The mechanism of a graphene growth was studied carefully. A lot of experimental parameters appeared to influence on the growth process of the carbon film. The dependences of the graphene layer number on the temperature, on the concentration of the methane in the gas mixture, on the gas pressure in the chamber, on the deposition time, on the heating and cooling rates have been measured.

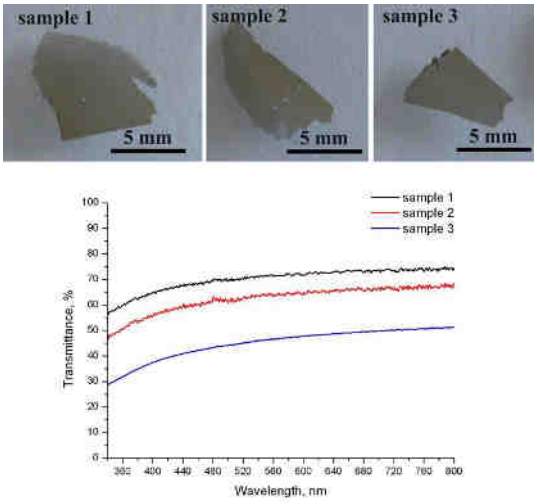

Fig.1. The optical absorption spectra of the different samples. The samples with numbers 1, 2, 3 contain 13, 17 and 26 graphene layers, correspondingly.

The samples were transferred onto SiO_2/Si substrate for the Raman measurements [2, 3]. The optical absorption was also measured for diagnostics of the properties of the prepared samples. A number of layers was estimated for each on the base of an absorbance of one layer of 2,3% [4].

The work was supported with RFBR– 10-02-00792 project and RAS research programs.

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"RAMAN SPECTRA OF CARBONACEOUS NANOMATERIAL "TAUNIT"

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Carbonaceous nanomaterial (CNM) "Taunit" constitutes the multy-walled nanotubes mainly with conic shape graphen layers. "Taunit" is promising material as vehicle for nanoscale size Pt-catalyst due to porosity and diameter distribution permanency of carbon nanofibres.

CNM "Taunit" used in this work is synthesized by MOCVD method. Raman spectra were recorded at room temperature using 325-, 514- and 633-nm lines of laser irradiation using microRaman system inVia Reflex Renishaw in backscattering configuration. The pristine sample and samples annealed at different temperatures were used for Raman measurements. Also sample functionalized by Pt-catalyst nanoparticles with the size distribution 3 - 6 nm was studied.

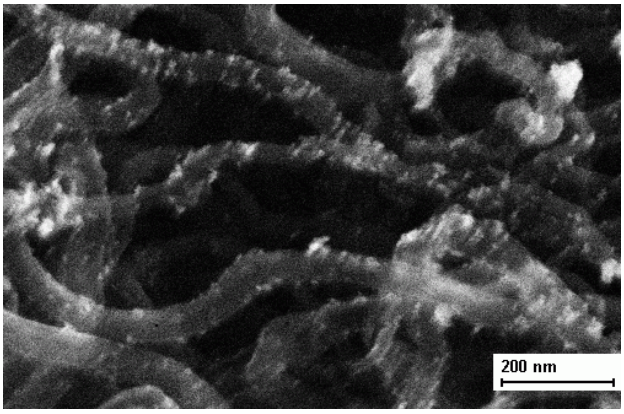

Fig.1. Carbonaceous nanofibres "Taunit with Pt-catalyst nanoparticles

The influence of annealing temperature on the Raman spectra of CNM "Taunit" was studied. It was found that "Taunit" belongs to poorly organized CNM but its crystalline structure ordering was observed with increasing the annealing temperature up to 500 ^{0}C. The ratios D- and G-bands (about 1350 and 1580 cm^{-1} respectively) were calculated to estimate crystal structure ordering of CNM "Taunit".

Also the influence of functionalization by catalyst nanoparticles was revealed. It is shown that Pt-catalyst precipitation on the surface of CNM "Taunit" leads to increasing of the defect band intensity due to appearance of some crystal lattice defects.

TEMPERATURE DEPENDENCE OF FIELD EMISSION FROM NANOGRAPHITE FILMS

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Nanographite film (NGF) materials exhibit outstanding field emission (FE) properties with low turn on field and high current densities [1-3]. Therefore they represent essential interest for vacuum electronics. However, mechanism responsible for this behavior remain unclear.

In the present work the dependence of field emission from nanographite films on temperature has been studied. Samples were obtained by chemical vapor deposition (CVD) method [3]. An example of SEM image of NGF is represented on Fig. 1. The field emission properties have been measured in flat diode configuration in vacuum better than 10^{-7}Torr. The cathode temperatures were ranged from 30 to 220^{o}C. The "turn-on" threshold fields for each temperature were determined carefully using method described in [1]. The obtained temperature dependence (Fig. 2) demonstrates little threshold reduction with heating above 200 ^{o}C. The possible mechanisms of the temperature dependence will be discussed.

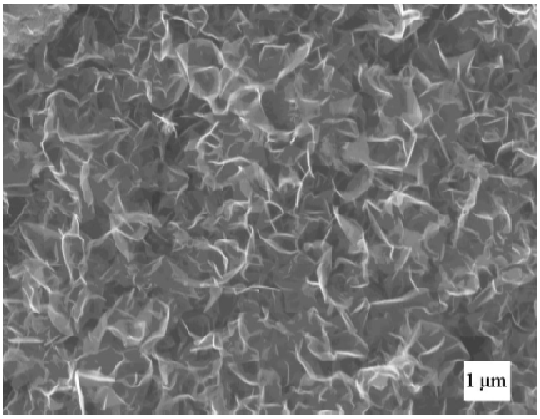

Fig. 1. Typical SEM image of NGF cathode surface.

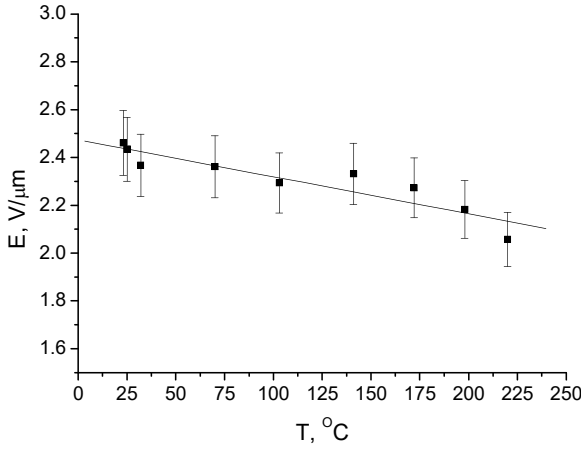

Fig. 2. FE "turn on" field dependence on temperature.

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APPLICATION OF NONLINEAR LIGHT SCATTERING IN NANOCARBON SUSPENSIONS FOR ADJUSTMENT OF LASER PULSE DURATION

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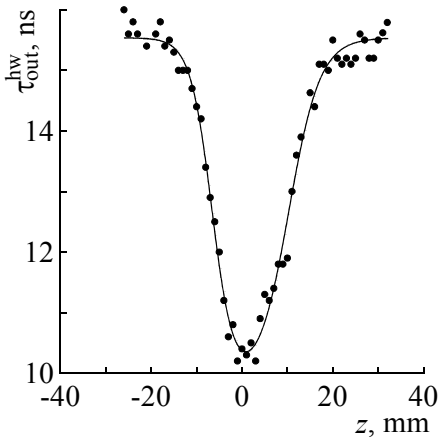
It is known that different methods may be used for adjustment of nanosecond laser pulse duration such as using the electro-optic switches, nonlinear absorbers, stimulated Brillouin scattering and stimulated Raman scattering. Here we present the new method which allows the nanosecond laser pulse duration to be changed smoothly.

We have directly demonstrated that mechanism of the optical power limiting (OPL) in aqueous suspension of multiwalled carbon nanotubes is the nonlinear light scattering [1]. This demonstration was realized by using a modified *z*-scanning scheme. Nonlinear scattering cuts off the trailing part of the incident laser pulse. Thus the full width at half maximum τ_{out}^{hw} of the transmitted laser pulse through suspension decreases with increasing (decreasing the coordinate $|z|$ of a suspension cuvette relative to the laser beam waist) of incident laser power density.

In our experiments we used the *z*-scan technique with a passively Q-switched YAG: Nd^{3+}- laser system (λ = 1064 nm, pulse energy ε_{in} = 0.3 mJ, pulse duration τ_{in}^{hw} = 16 ns). The focal length of the collecting lens was 100 mm, and the beam waist diameter was $2r_0$ = 100 μm. We investigated the dependence of τ_{out}^{hw} on *z* in an aqueous suspension of multiwalled CNTs which were synthesized by the electric-arc evaporation of graphite (most nanoparticles had a diameter 15 – 20 nm and a length less than 1 μm).



Experimental results presented in Figure show that the scanning a cuvette with aqueous suspension of multiwalled carbon nanotubes along the optical axis is accompanied by smooth change of nanosecond laser pulses duration transmitted through suspension. At z = 0 the duration of transmitted laser pulse is $\tau_{out}^{hw} \approx$ 10 ns. Thus incident YAG: Nd^{3+}- laser pulses of 16 ns duration have been smoothly adjusted in the range of 10 - 16 ns.

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FORMATION OF HYBRIDS FROM CARBON MATERIALS AND MOLYBDENUM SULPHIDES

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Combination of low dimensional carbon nanostructures, possessing high electrical conductivity, with semiconducting nanoparticles allows creating new class of hybrid materials with unique electronic, optical and luminescent properties. Hexagonal structure of graphitic materials and molybdenum sulfide allows jointing these compounds in a hybrid. Two methods based on hydrothermal and high temperature annealing of components were proposed to cover multiwall carbon nanotubes with MoS_2 [1-3]. Such composites can be useful for friction reduction [3] and possess interesting electronic properties [4].

In this work we are presenting our investigations in the field of creation hybrid structures based on molybdenum sulfides and different carbon materials (arc discharge multiwall carbon nanoparticles, CVD-produced carbon nanotubes, and exfoliated graphite). Hybrids were prepared by different techniques, which allow depositing of various molybdenum sulfide forms on carbon surface. First technique is a high temperature annealing of MoS_3 with pristine carbon material, the second one is autoclave method realized hydrothermal decomposition of thiourea and ammonium molybdate at 235°C. The obtained samples were studied using high resolution transmission electron microscopy (HRTEM), energy dispersion spectroscopy, x-ray diffraction (XRD), and Raman spectroscopy. It was found that the form and composition of molybdenum sulfide nanoparticles deposited on the carbon surface depend on the structure of initial carbon materials and annealing temperature. Thus, varying the annealing temperature we were able to produce MoS_2, Mo_2S_3, or Mo_3S_4 covering on the exfoliated graphite. Formation of two latter species proceeds much faster if molybdenum sulfide is supported by graphitic substrate.

This work was financially supported by the Russian foundation of base research grant No. 10-03-00696-a. We are grateful to Mr. A.V. Ishchenko for the TEM measurements.

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THE USE OF NH_3 TO PROMOTE GROWTH OF SINGLE-WALLED CARBON NANOTUBES WITH HIGH HELICITY

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Single-walled carbon nanotube (SWCNT) [1] is a promising material since it exhibits unique and important mechanical, optical and electronic properties [2]. SWCNT is either metallic or semiconducting depending on its diameter and chiral angle or, equivalently on its chirality (*n,m*) [3]. Application-oriented research on carbon nanotubes requires reliable control over the growth process for nanotubes with desired chirality. In this contribution we report a novel process for growth of single-walled carbon nanotubes (SWCNTs) with a narrow chiral angle distribution. SWCNTs were synthesized by continuous floating catalyst chemical vapor deposition (CVD) based on ferrocene vapor decomposition in a carbon monoxide (CO) atmosphere at a certain temperature [4]. The chiral structures of the nanotubes were determined by means of electron diffraction analysis. It was discovered that, by introducing a small amount of NH_3 in the synthesis process, the chiral angle distribution of as-grown SWCNTs can be promoted to a constricted range with about 90% nanotubes having high helicities (20°-30°), and 50% in the range 27°-29°. This finding represents a significant step towards chiral-selective growth of SWCNTs

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NON-LITHOGRAPHIC PATTERNING OF CARBON NANOTUBE NETWORKS FOR ELECTRONIC APPLICATIONS

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Carbon nanotube networks (CNTNs) have been widely studied due to their potential for low-cost applications in electronics, enabling large area coverage, structural flexibility and low-temperature processing. The successful implementation of CNTNs in devices requires the ability to pattern the networks into various features at desired locations on the substrate. Owing to the earlier demonstrated efficient and density-controlled dry deposition method of SWCNTs at room temperature directly from the aerosol synthesis reactor onto any type of substrate [1, 2], we were able to achieve the direct CNTN patterning simultaneously with the deposition process in gas phase by means of a shadow mask and fabricate CNTN-based transistors eliminating photolithography or etching processes. The mask during the whole fabrication process remains intact on the substrate, allowing precise electrode-CNTN channel alignment.

The CNTN patterning method is based on electrodynamic focusing concept for charged aerosols [3]. Due to the spontaneous charging phenomenon of SWCNT bundles [4], charge is accumulated on the mask surface during the CNT deposition, modifying the applied electric field to produce electrostatic lenses around the mask opening. Thus CNTs are efficiently focused into the mask opening and onto the collecting substrate, producing feature sizes of the obtained patterns smaller than the ones on the mask. The experimental results were verified by numerical simulations of electric field distribution. Therefore, by controlling the electric field-induced motion of CNTs, we can selectively deposit CNTNs and scale down the features of CNT patterns, overcoming the mask resolution limits, which is advantageous for various electronic applications.

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Friday, August 6

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Size-effect in field electron emission from carbon nanomaterials

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A broad range of carbon materials (graphite and glassy carbon, DLC, CVD diamond, nanocomposites, nanotubes and some others) were investigated. Electron emission was studied using multiple-probe set-up and scanning tunneling field emission microscope (STFEM) which can produce overlapping maps of surface morphology, local emission curves, signal proportional to the value of the surface potential barrier and local electroresistivity with resolution about 1 nm.

Low thresholds for field electron emission (≈0.5-2V/μm) were detected only for nanostructured materials and such emission takes place from conductive nanophase of carbon, surrounded by an insulator or vacuum [1, 2].

This data can not be explained by the electrical field enhancement alone. It has been proposed [3] that low threshold emission effect can be interpreted on the basis of the assumption that nanosized structures, being low dimensional quantum objects, have a lower potential barrier for electron tunneling into vacuum as compared to the bulk material. Estimations made for two-dimensional quantum well (ultra thin film) confirmed such a mechanism and gave a dependence of work function of electrons variation

$$\Delta\Phi = \frac{K}{h^2} \qquad (1)$$

where K=const and h- film thickness.

To confirm the validity of such a model special experiments were performed [4]. Hard DLC films were deposited on Si substrates and thermally annealed in vacuum at temperature $\leq 620^0$C. That allowed to obtain highly graphitized (sp^2 portion close to 100%) conductive films with thickness 7-117nm and surface roughness 0.15nm. The principal experimental result is presented on Fig.1 and is in good functional agreement with the theoretical prediction (1).

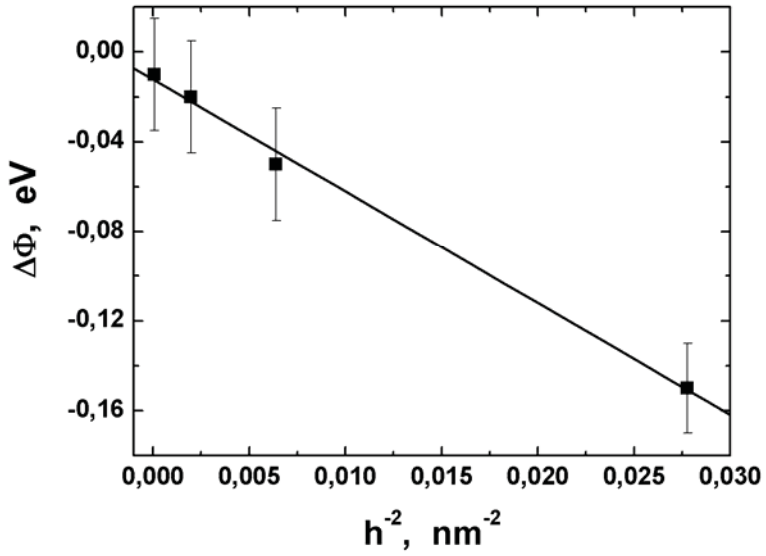

Fig. 1. The work function of electron variation **ΔΦ** vs. the film thickness **h** plot.

Note, that similar results we also obtained earlier in [5] with carbon nanoobjects having symmetry close to zero-dimensional.

This work was supported by RFBR grant #09-02-01029.

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Thermionic and Photostimulated Electron Emission from Nanostructured Carbon and Diamond Materials

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Electron sources are utilized in a wide range of applications ranging from electron guns, high power telecommunications to space propulsion and direct energy conversion. Diamond acquires its electron emissive properties due to the negative electron affinity (NEA) of its surfaces as well as the introduction of dopants.

Thermionic electron emitters based on diamond require control of the surface electron affinity, doping levels and concentration, and band bending. It is now well established that H-terminated diamond surfaces result in a negative electron affinity where the vacuum level is located below the conduction band minimum (CBM). Doping with nitrogen or phosphorus results in donor levels at 1.7 or 0.6 eV below the conduction band. It appears that optimized nanocrystalline films result in a low film resistance and control of band bending. The thermionic electron emission has been measured from engineered multilayered structures of nitrogen doped, nanocrystalline diamond films. The temperature dependence of the electron emission can be analyzed using the Richardson – Dushman equation, and optimized films display a low work function of ~ 1.3 eV and a significant Richardson constant of 7 $A/cm^2 K^2$. Thermionic electron emission commences at temperatures lower than 250 ºC, and at a low temperature of ~ 450 ºC a significant electron emission current density of 1 mA/cm^2 was observed.

Here, we present results on electron emission from nitrogen and phosphorus doped diamond films and combine both the thermionic emission and photo-induced. The results will compare the processes for thermionic and photo induced electron emission.

ULTRAFAST LASER-ASSISTED ELECTRON EMISSION

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Nanostructured graphite films (NGF) have emerged as a prospective material for the manufacturing of cathodes in the field electron emission devices [1]. We have reported also enhancement of the field emission by irradiation of NGF by nanosecond laser pulses [2], which increase the temperature of the cathode surface. Since the laser pulse length is longer than the electron-phonon interaction time, the optical excitation resulted in the heating of the lattice and conventional thermionic emission occurred. However, the excitation of the cathode with femtosecond pulses allows one to increase the temperature of the electronic sub-system alone leaving the lattice unaffected. Here we demonstrate anomalously high electron current density produced by NGF cathodes excited by ultrashort light pulses at relatively low applied voltage.

In order to investigate properties of hot electrons in NGF, we measured the electron emission as a function of the energy and duration of light pulses produced by Ti:Sapphire femtosecond oscillator with amplifier (repetition rate 50 Hz, pulse energy up to 1.2 mJ, pulse duration can be tuned by a pulse stretcher from 55 fs to 300 fs).

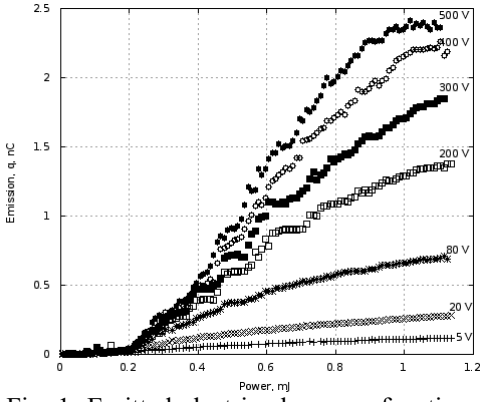

Fig. 1: Emitted electric charge as function of the laser pulse energy for different applied voltage

In the electron emission experiment, we employed a vacuum diode with NGF cathode and ITO anode separated by 0.5 mm gap. Field emission threshold for this diode was as low as 1000 V. Due to a finite capacity of measurement setup the response time of the system was about 2 ns, i.e. it was much longer than the electron subsystem relaxation time $\tau_e \approx 1$ ps. However we can estimate the emission current density by measuring the total electric charge transferred from cathode to anode.

We demonstrate that the electric charge emitted by the NGF cathode can be as high as 2.5 nC at excitation pulse energy 1.2 mJ, pulse length about 60 fs and applied voltage of 500 V (see Fig. 1). Our measurements show also that the emitted charge decreases with increasing of laser pulse duration.

The obtained results indicate that NGF cathodes have strong potential in the development novel vacuum electronic devices including pulsed X-ray sources.

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EFFECT OF RESIDUAL GASES ON FIELD EMISSION FROM NANOGRAPHITE FILMS

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In the present work the dependence of field emission (FE) from nanographite (NG) films on the pressure of the residual gases in the vacuum chamber has been studied. The films were obtained by the plasma enhanced chemical vapor deposition method. It is remarkable that the FE properties demonstrate long-time stability at operation of NG cathodes with pressure better of 10^{-5} Torr. With the pressures exceeding 10^{-5} Torr the decrease of the FE current has been observed at a constant applied voltage up to level depending on the pressure. The duration for the current drop was increased with the gas pressure (Fig. 1). A partial recovery of the current has been observed after pumping out of the measuring cell to the original pressure level of 10^{-5} Torr. The time dependencies of the current drop show two parts with different characteristic rates (Fig. 2). At the pressure value exceeding 10^{-2} Torr emitted electrons produce intense ionization of the residual gas. These ions create main part of the total current measured between the cathode and anode.

The experimental observations are explained by the action of the ion bombardment and adsorption/desorption processes at the surface of the NG films during field emission measurements.

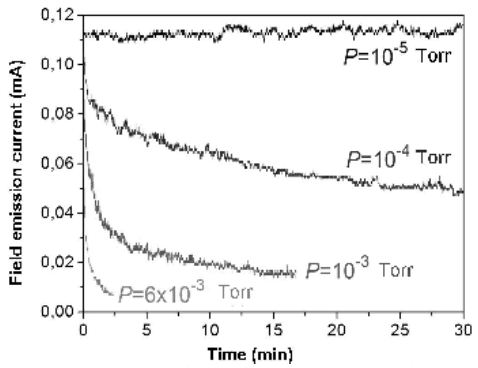

Fig. 1. FE current dependence on time at different pressure values (at dc voltage of 1200 V).

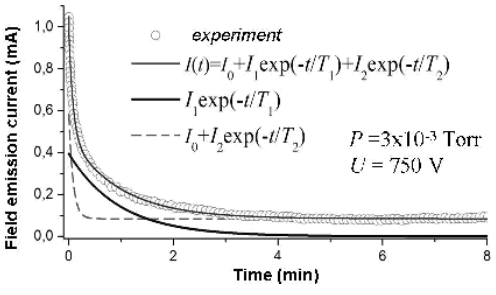

Fig. 2. Experimental FE current dependence on time at $3x10^{-3}$ Torr and the approximation curves.

ELECTROMECHANICAL SELF-OSCILLATIONS OF CARBON NANOTUBE FIELD EMITTERS

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Field emitters based on carbon nanotubes (CNT) are known as efficient sources of electrons which can provide intense and stable electron beams under the action of applied electric field. High efficiency of the field emission is resulted essentially from high aspect ratio of CNT having micrometer size length at nanometer scale diameter. By having this "wire-like" geometry and one of the highest mechanical strength CNT can sustain considerable elastic deformations induced by the action of the strong electrical ponderomotive forces during field emission. The elastic deformations lead to various electromechanical effects which should be taken into account during investigation of field emission.

We report here the observation of the electromechanical self-oscillations during emission of electrons from flexible field emitters made of carbon nanotubes. Under the action of a constant voltage applied between a CNT cathode and a flat anode the stable mechanical and emission current oscillations have been observed. The effect was investigated in dependence on geometrical characteristics and voltage applied. We propose an empirical model described by the equations system of the mechanical motion and electrical processes. The model provides a qualitative agreement of the experimental and theoretical results. It is shown that observed phenomenon may be used for the generation of the high frequency electromagnetic waves by using the electromechanical systems with field emitters of nanometer size.

CATALYST FREE GROWTH OF CARBON NANOTUBE FOREST

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Carbon nanotubes (CNT) attract great interest for both fundamental and applied studies. The most common methods of CNT synthesis include usage of nano-sized metal catalytic particles. The presence of metal impurities is unacceptable or undesirable in many cases. Additional purification treatments are used to eliminate the catalyst particles. However, the use of such treatments often leads to formation of structural defects in nanotubes, which may be undesirable again. In this work we present the results of experimental investigations aimed to develop catalyst-free process for CNT synthesis. A chemical vapor deposition technique was used to provide condensation of carbon from gaseous phase activated by a direct current discharge on Si substrates isolated from an immediate contact with plasma.

Deposition process was conducted without adding any catalyst particles. By adjusting the deposition parameters we were able to produce film material of densely packet oriented CNT (i.e. CNT forest). Detailed investigation of obtained nanotubes was carried out by Raman spectroscopy, scanning and transmission electron microscopy, elemental analysis (energy dispersive X-ray and electron energy loss spectroscopy). It was shown that CNTs contain 4 to 7 layers, are well-aligned and have no metal impurities (see Figs. 1, 2). The possible mechanisms of the catalyst-free carbon nanotube formation are discussed.

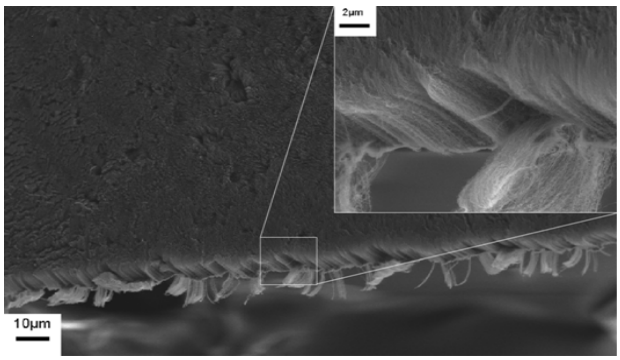

Fig. 1. SEM images of the CNT forest, obtained by the catalyst free CVD.

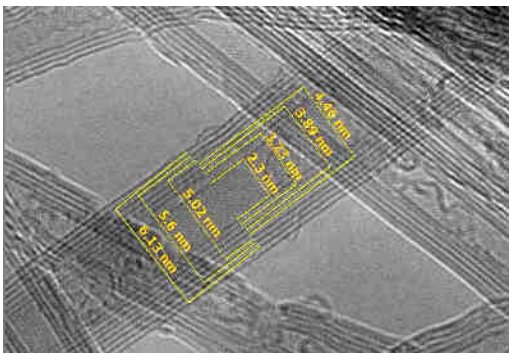

Fig. 2. HRTEM image of the CNT grown by the catalyst free CVD.

GAS PHASE FLOATING CATALYST SYNTHESIS, FORMATION MECHANISM AND CHARACTERIZATION OF NITROGEN-DOPED SINGLE-WALLED CARBON NANOTUBE FILMS

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We will present a method to synthesize N-doped SWCNTs using a gas phase floating catalyst reactor. The method allows depositing the as-grown material directly on various substrates in a simple continuous process using a resistively heated iron wire/CO/ ammonia system. No solution dispersion or processing is used to preserve the intrinsic properties of the material.

To study the mechanisms of doping, spin-polarized periodic density functional theory (GPAW code) was employed. The bonding and chemistry of CO, NH_3 and their fragments on a Fe55 icosahedral cluster was considered. Possible dissociation paths for NH_3 to atomic nitrogen and hydrogen were identified. The calculated lowest reaction barrier is comparable to an experimentally determined value (0.45 eV) obtained by FTIR and mass spectrometer measurements. The CO dissociation barrier (0.63 eV) is lower than on most of the studied Fe surfaces. Possible paths for C-C and C-N bond formation were also identified and found to be barrierless.

Optical absorption and Raman spectroscopy were performed on samples synthesized with varying amounts of ammonia. The nitrogen content was examined with XPS, showing that a controllable doping level was achieved. Additionally, TEM/EELS observations were combined with STM/STS in order to locally understand the role of N atoms at the dopant sites. A well-structured photoluminescence signal was observed, demonstrating that low enough doping level preserves the electronic structure of the SWCNTs. Finally, we studied the electrical properties of the films for possible application as transparent conductors and thin film transistors.

[1] T. Susi et al., submitted (2010)

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