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Abstract BOOK

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Yury Svirko
Dmitry Lyashenko

Joensuu, Finland

3 - 9 August 2008

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NPO2008 Schedule-at-a-Glance

	Monday, 4 Aug	Tuesday, Aug 5	Wednesday, Aug 6	Thursday, Aug 7	Friday, Aug 8
7:00-9:00	*Breakfast*	*Breakfast*	*Breakfast*	*Breakfast*	*Breakfast*
9:00-10:30	Philippe Lambin	Christian Thomsen	Serge Lefrant	Werner Blau	Robert Nemanich
10:30-11:00	*Coffee Break*	*Coffee Break*	*Coffee Break*	*Coffee Break*	*Coffee Break*
11:00-12:30	Esko Kauppinen	Shiniji Hayashi	Brigitte Trétout	Andrea Ferrari	Alexander Obraztsov
12:30-14:00	*Lunch*	*Lunch*	*Lunch*	*Lunch*	*Lunch*
14:00-15:30	Annik Loiseau	Sergey Maksimenko	**Bus trip to Koli National park**	Elena Obraztsova	Oral presentations
15:30-16:00	*Coffee Break*	*Coffee Break*		*Coffee Break*	*Coffee Break*
16:00-16:30	Andrey Chuvilin	Lubov Bulusheva		Oral presentations	Alexander Okotrub
16:30-17:15	Oral presentations	Oral presentaions		Oral presentations	Conclusion
17:15-18:00					
18:00-18:30	*Dinner*	*Dinner*			**Boat trip**
18:30-19:30	*Dinner*	*Dinner*	*Dinner*	**Workshop dinner**	
19:30-20:00		Poster presentations	Poster presentations		
20:00-21:00	**Welcome party**	Poster session I	Poster session II		
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21:30-22:00					

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Monday, August 4

Electronic structure, optical properties, and plasmonics of carbon nanotubes

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The pace of research on carbon nanotubes has been considerably enhanced by the discovery of the extraordinary electronic properties predicted for single-wall nanotubes (SWNTs). These properties are very sensitive to the nanotube atomic structure, namely its diameter and chiral angle or, conventionally, to the wrapping indices n and m that label the arrangement of the honeycomb atomic lattice on a seamless cylinder. It was readily predicted that when the difference n - m between the wrapping indices is a multiple of 3, the nanotube is metallic, otherwise there is a semiconducting gap in its band structure. These properties, and others, can be deduced easily by a simple zone folding of the π-bands of graphite, as demonstrated in this tutorial.

The extreme sensitivity of the electronic properties to the atomic structure of the nanotube is a consequence of the quantization of the π-electron wavevector imposed to the wavefunction by the cyclic boundary condition around the circumference. It follows that a slight change of the couple (n,m) can result in the SWNT being either metallic or semiconducting. Possible applications of nanotubes in nano-electronic devices will have to accommodate and exploit that property.

Optical properties of the nanotubes are direct consequences of their electronic band structure, with the remarkable set of van Hove singularities, typical of one-dimensional systems. Within the framework of the joint density of states, a universal expression of the nanotube optical absorbance can be deduced from the positions of the van Hove singularities. Other, more refined models will be developed in the course of the lecture to derive a dielectric function of the nanotubes. This will allow us to introduce the concept of π-plasmon in these carbon nanostructures, namely a collective excitation of their π electrons.

Carbon NanoBuds^{TM} – a novel nanomaterial: synthesis, structure, field emission and transport properties

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We present synthesis, structure and field emission properties of a novel hybrid carbon nanomaterial, NanoBuds^{TM}, combining fullerenes and single-walled carbon nanotubes (CNTs) . NanoBuds consist of fullerenes attached to the *outside* surface of CNTs, i.e. nanotubes are functionalized with fullerenes (1). Two floating catalyst methods for their selective synthesis have been developed, using pre-made iron catalyst particles by a hot wire based PVD method or grown *in situ* via ferrocene vapour decomposition in the presence of CO and trace amounts of H_2O and CO_2. TEM images show spherical structures i.e. fullerenes at the surface of the tube. Their spherical nature was confirmed by tilting samples within a HR-TEM. Strong bonding of fullerenes to anotube surface was shown by in-situ Cs-corrected TEM observations. Statistical size measurements on the basis of HR-TEM images revealed that the majority of fullerenes consists of C_{42} and C_{60}. Interestingly, evidence of C_{20} fullerenes, the smallest possible dodecahedra is found. Individual nanobuds were observed both by HR-TEM and micro-Raman, both showing fullerenes at tube surfaces and diving chirality information for the tubes. The main peaks in MALDI-TOF spectrum are attributed to C_{60} ($C_{60}H_2$, $C_{60}H_2O$) and C_{42} ($C_{42}COO$) fullerenes. Accordingly, fullerenes are attached to CNTs via either oxygen (preferable for fullerenes larger than C_{54}) or carboxylic (for smaller fullerenes) bridges, which was confirmed by FT-IR measurements. EELS observations with TEM also showed the existence of oxygen. Scanning tunneling microscopy (STM) and spectroscopy (STS) measurements of samples deposited on Au(111) substrate confirmed the covalent nature of fullerene bonding to the tube. Atomistic density-functional-theory based calculations showed that systems composed of fullerenes and nanotubes with single vacancies covalently functionalized through ester groups can indeed exist. In-situ deposited i.e. non-purified planar NanoBud mats showed stable cold electron field emission with a current density of 189 $\mu A/cm^2$ at 1.26 V/µm. The threshold voltage was about 0.6 V/µm, compared to over 2 V/µm for similarly produced planar nanotube mats. We discuss sheet conductivity of nanotube and –bud films, as well as their optical absorption characteristics. Also, we discuss dry, ambient temperature deposition methods of thin films for transparent electrode and TFT-FET device manufacturing.

1. A. G. Nasibulin, P. V. Pikhitsa, H. Jiang, D. P. Brown, A. V. Krasheninnikov, A. S. Anisimov, P. Queipo, A. Moisala, D. Gonzalez, G. Lientschnig, A. Hassanien, S. D. Shandakov, G. Lolli, D. E. Resasco, M. Choi, D. Tománek, and E. I. Kauppinen, (2007) A Novel Hybrid Nanomaterial, *Nature Nanotechnology* **2**(3), 156-161

Investigation of the structure of the nanotubes by transmission electron microscopy

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Transmission Electron Microscopy (TEM), thanks to which discovery of carbon nanotubes has been made possible, is a major tool for studying structural properties of individual nanostructures such as nanotubes. The objective of this course is to review different modes available in a TEM able to provide different kinds of information on the nanotube structure. The modes in turn are diffraction, high resolution imaging and electron energy loss spectroscopy. In the two first ones, electrons are transmitted and elastically diffracted by the electrostatic potential of the atoms and provide information on the spatial arrangement of these atoms, including the determination of the atomistic structure and the identification of some structural defects. The third one uses electrons which have lost a certain part of their energy during their transmission through the material, the energy losses being due to the excitation, for atoms of the material, of electronic states above the Fermi level. Energy losses related to core states provide an elemental analysis of the material, including the quantification of the concentration of a given element, its spatial distribution and its chemical local environment. Energy losses can also be related to electrons close to the Fermi level, allowing one to study the dielectric function of the material and to investigate interband transitions or plasmons.

The course will first introduce these different modes and then consider their application to the nanotubes, by emphasing different concrete situations. It will be organised as follows:

1) Structural analysis by elastic scattering techniques :

- Theory of the elastic propagation of rapid electrons through a crystallized material
- Image formation : nature of the contrast and its dependance to the scattering characteristics of the atoms,
- Effects of the optical aberrations of the microscope on both the image contrast and resolution, and their modelization by a transfer function
- Imaging nanotubes : analysis of the contrast and of its relationship with the atomistic structure of the nanotube depending on the transfer function of the microscope.
- Diffraction by a nanotube and its use for determining helicity and (n,m) indices

2) Structural analysis by electron energy loss spectroscopy (EELS)

- Description of the different losses : absorption edges (above 50 eV) due to excitation of core states and low losses (0 – 50 eV) due to plasmons or inter-band transitions
- Elemental analysis from absorption edges : i) principle of the elemental quantification, ii) chemical mapping using either the spectrum-imaging technique in a STEM or energy filtered imaging in a TEM, iii) use of the energy loss near edge structure (ELNES) for studying and mapping the chemical bondings
- Low energy losses: description of two complementary approaches for measuring the dielectric function of a nanotube and determining the nature of the excitations.

APPLICATION OF LOW VOLTAGE Cs-CORRECTED TEM FOR NANOCARBON MATERIALS

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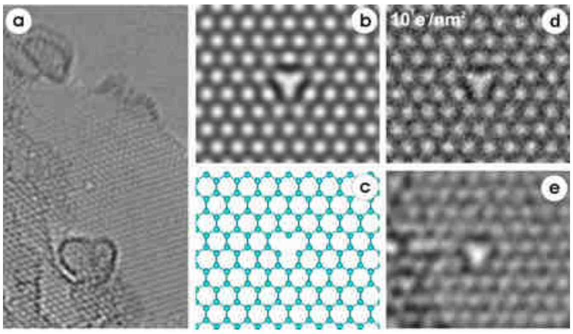
Theory, state of the art and prospective of aberration corrected low voltage transmission electron microscopy in application to carbon materials will be discussed.

Being one of the main methods for studying the atomic structure of carbon materials, high resolution TEM suffers from a serious flaw as the energy of electrons, necessary to obtain atomic resolution (200-300 keV), is far above the kick-off damage threshold for graphitic carbon (about 60 keV) [1], which means that carbon nanostructures are always observed more or less damaged by electron beam. Practical implementation of Cs correctors in the last decade [2] opened the possibility to decrease acceleration voltage of the microscopes significantly, yet preserving the resolution at reasonable level. This opens a possibility for direct observation of pristine structure of nanocarbons at atomic level.

We present first examples of application of 80kV electron microscope with imaging Cs corrector for studying carbon nanotubes, peapods and graphene. We show that nano-structures composed of graphitic carbon are stable under the conditions of observation for more than 30 minutes, which opens the possibility for monitoring of single atom dynamics, diffraction studies and EELS measurements without radiation damage induced by the electron beam. Visualization of one single carbon atom within a graphene network is show. Direct visualization of defects within the graphene network is demonstrated (see Figure). Time resolved imaging of temperature induced evolution of peapods illustrates a perspective for direct observation of chemical reactions on atomic level.



(a) experimental image of a single graphene layer with a monovacancy, (b) calculated image of a monovacancy, (c) atomic model, (d) calculated image for the dose $10^7 e^-/nm^2$, (e) extraction from experimental image.

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COMBINED RAMAN SPECTROSCOPY AND TRANSMISSION ELECTRON MICROSCOPY STUDIES OF A NANOBUD STRUCTURE

Ying. Tian, Delphine Chassaing, Albert G. Nasibulin, Paola Ayala, Hua Jiang, Anton S. Anisimov and Esko I. Kauppinen*

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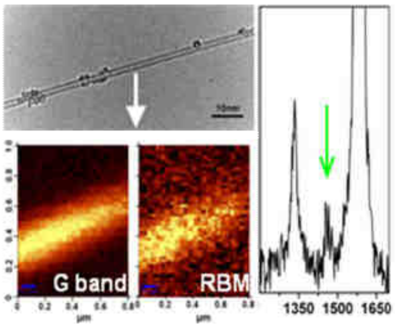
Fullerenes and carbon nanotubes (CNTs) have attracted a great interest in the research community due to their remarkable properties and potential applications. Recently, we have discovered a novel hybrid material that combines fullerenes and single-walled carbon nanotubes (SWCNTs) into a single structure in which the fullerenes are covalently bonded to the outer surface of the SWCNTs, called NanoBuds.[3] This new material showed a high cold electron field emission efficiency thus making it attractive for many electronic applications, e.g., flat panel displays. In the previous reports [1,2], we have confirmed the NanoBud structure by transmission electron microscopy (TEM), Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF), UV-vis absorption spectra, scanning tunnelling microscopy (STM) and spectroscopy (STS) measurements. However, due to the low symmetry and wide distribution of fullerenes in the NanoBud samples, until now, no feature from fullerenes has been detected with Raman spectroscopy.

In this work [3], we present a combined Raman and TEM study of an individual freestanding NanoBud structure. By focusing on the single NanoBud structure instead of a bulk powder sample, allowed us to observe for the first time the characteristic features of both SWCNT and fullerenes in the Raman spectrum. The Raman features corresponding to the typical vibrational modes of fullerenes were observed in the range of 1440-1480 cm^{-1}. Moreover, the atomic structure of the CNT was determined independently by electron diffraction (ED) and Raman spectrocopy.



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Structural and optical properties of diamond nanotips

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Chemical vapor deposition techniques (CVD) have been developed to obtain single-crystal diamond tips. The diamond growth occurs on silicon substrates from methane-hydrogen gas mixture activated by a direct current discharge. Properties of the tips were investigated with Raman spectroscopy, SEM, HRTEM and optical spectroscopy.

SEM analysis shows that, the crystallites have almost identical shape of regular square pyramid with angle at vertex of about 5°- 10°. Their length and base size are defined by the parameters of CVD process and are in range from hundreds of nanometers to tens of micrometers. These diamond tips are produced in form of thin film consisting of crystallites with the apexes directed to substrate surface. The crystallites are aligned preferentially perpendicularly to the substrate plane and can be easily released from the film individually.

High crystalline ordering of the tips is confirmed by Raman (see fig. 1), electron diffraction and HRTEM data. HRTEM imaging also shows that radius of curvature of the diamond tip apex is less than 5 nm. In particularly, the most characteristic features of the Raman, evidencing single crystal structure of the diamond tips are presence of an intense peak at about 1330 cm^{-1} and absence of Raman lines in range, corresponding to graphite-like and amorphous carbons (around 1350 and 1580 cm^{-1}). The 1330 cm^{-1} “diamond” line is very narrow (about 3.2 cm^{-1}) which is specific also for perfect crystals only.

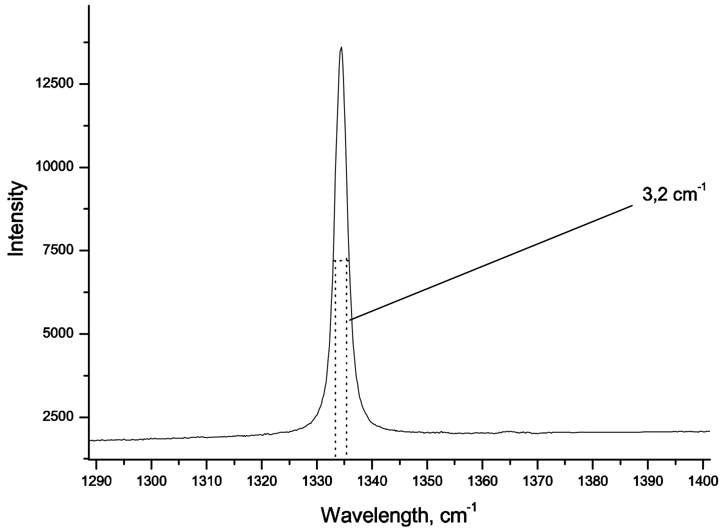

Fig. 1. Typical Raman spectrum of diamond nanotips.

MODELING of VARIATION of ELECTRONIC STRUCTURE of GRAPHITE CLUSTERS INDUCED by VARIATION of GRAPHENE LAYER NUMBER

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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 surfaces in graphite with a variable number of layers (from 1 up to 5). The density functional theory with a pseudo-potential method has been used for the calculations. Modeling has shown a splitting of the dispersion surfaces corresponding to π-electrons while the number of layers increases *(Fig.1)*.

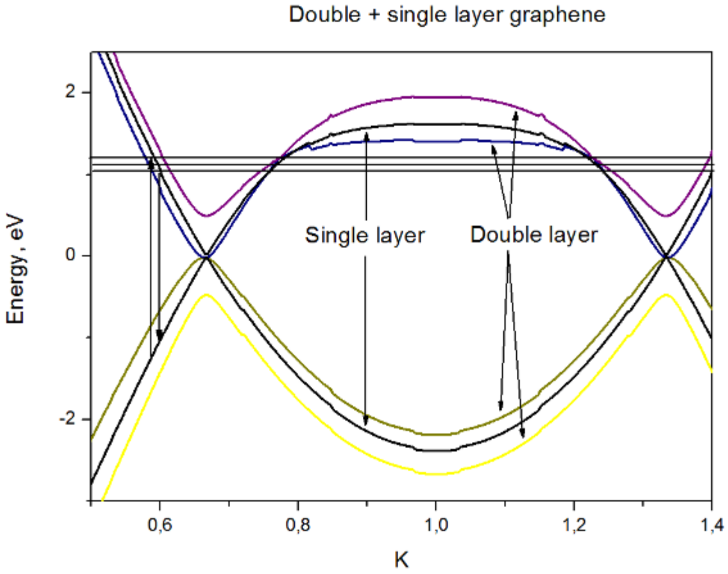

Fig.1. Electron energy dispersion for one graphene layer and for two graphene layers(modeled with a density functional technique).

An acceptable coincidence has been obtained between the results of modeling and the experimental data, observed earlier [1]. One of the applications of this modeling is an interpretation of the resonant Raman spectra of graphite clusters with a small number of graphene sheets.

The work is supported by RFBR 07-02-01505 and RAS research programs.

[1] E. A. Obraztsova, A. V. Osadchy, et al. «Statistical analysis of atomic force microscopy and Raman spectroscopy data for estimation of graphene layers number», *Book of abstracts of XXII International Winterschool on electronic properties of novel materials”, Kirchberg (Austria), March 2008, Th-28, p. 147.*

Tuesday, August 5

Raman Spectroscopy of Carbon Nanotubes and Semiconductor Nanorods

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We give an overview over recent theoretical and experimental results on carbon nanotubes and on semiconducting nanostructures. Resonant Raman and photoluminescence-excitation spectroscopy have developed into one of the most frequently used analytical methods for nanotubes and nanowires [1]. They are able to straightforwardly determine structural parameters and hence optical and transport characteristics contact free and down to the single-molecule level. Without much specialized equipment it is possible with Raman scattering to quickly identify a semiconducting or metallic nanotube, which is important for the technological application of nanotubes.

In the optical spectrum it has become clear that excitons with large binding energies (several 100 meV) determine the emission energies for the second and higher transitions[2]. Excitons are largely unscreened due to the one-dimensional nature of nanotubes. We discuss the electron-phonon coupling, the strengths of the Raman signals of the same tubes for the first and second optical transitions, exciton resonances in semiconducting nanotubes, and Fano resonances in metallic nanotubes. Recently it has become possible to identify the diameters of CdSe nanowires and nanorods[4] via their radial breathing-mode frequencies; we will compare theoretical and experimental results on this system.

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Synthesis and Optical Properties of Carbon Onions and Carbon Linear Chains

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Among carbonaceous nanomaterials, carbon onions and carbon linear chains still remain unexplored. Based on results of our recent studies, I would like to discuss the synthesis and optical properties of them. Mass production of carbon onions is possible by thermal annealing of nanodiamonds in high vacuum. Starting from nanodiamonds 5nm in diameter, we can obtain carbon onions having nearly the same size. The onions show optical extinction peak in the UV region, which can be well reproduced by theoretical calculations based on a core-shell model. By tuning the parameters in the model to those appropriate in space, we succeeded in reproducing the interstellar extinction bump around 217nm.

sp-carbon linear chains are mass produced by laser ablation of carbon targets in liquids. We could get solutions of size-separated linear chains by high performance liquid chromatography, which allowed us to study the chain-length dependence of Raman spectra. Systematic changes of normal Raman spectra and surface-enhanced Raman spectra as a function of the chain length could be observed.

Electromagnetic waves in carbon nanostructures

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A great progress has been achieved during last two decade in the synthesis and fabrication of different nanostructured artificial materials with fascinating mechanical, electronic and optical properties irreducible to properties of bulk media. Accompanied by the impressive parallel development of the characterization techniques and measurement instrumentation, this process necessitates the revision of traditional concepts of physics and chemistry of condensed matter, adapting them to peculiarities of the nanoworld and significantly extending our knowledge of the nature of solids and our capabilities to control their properties. Signalized by the prefix *nano-* these peculiarities define the development of a variety of new scientific and technological branches, such as nanomechanics, nanoelectronics, nanooptics, nanophotonics, nanosensorics, *etc*.

Following this general trend, a research discipline – ***nanoelectromagnetics*** – is introduced as a synthesis of macroscopic electrodynamics and microscopic theory of electronic properties of different nanostructures. The approach is exemplified by carbon nanotubes (CNTs) and briefly touches upon other nanocarbon forms.

The method of effective boundary conditions is shown to be a universal tool for the study of electrodynamic problems of nanotubes. A set of physical effects, which emerge from the interaction of light with different nanocarbon structures and which are due to characteristic sizes of objects, is presented. Linear electrodynamics of nanotubes, nonlinear optical effects in nanotubes and foundations of quantum electrodynamics in nanotubes are discussed. A strong slowing down of surface waves in CNTs is demonstrated and the concept of nanotube as a surface wave nanowaveguide in the infrared and terahertz range is presented. Antenna properties of CNTs and CNT bundles are described and the thermal radiation of isolated CNT is demonstrated to be strongly different from the black-body radiation. The idea of the CNT as monomolecular analog of free electron laser is proposed and discussed. The high-efficient generation of high-order harmonics in nanotubes exposed to strong pumping field is predicted. Experimental results on the third-order harmonic generation in nanotube ensemble is compared with theoretical predictions. The formalism of electrodynamics of lossy dispersive media is applied to the problem of spontaneous radiation of an excited atom in the carbon nanotube. First results on measurements of the attenuation of electromagnetic waves in onion-like carbon (OLC)–based polymer films on a substrate are reported in the microwave frequency range. The measurements demonstrate potentiality of OLC-based composites as basic components for wideband electromagnetic wave absorbing materials.

STRUCTURE AND ELECTRONIC STATES OF DEFECTS IN CARBON NANOTUBES

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Carbon nanotubes are generally not free of defects. Four kinds of defects can be recognized in graphitic network: non-hexagonal rings (topological defects), vacancies, adatoms, and substitution atoms. The defects are formed during the synthesis or in the result of any action (purification, bombardment, implantation, etc.). The direct observation of topological and vacancy defects could be made using transmission electron microscopy (TEM) or scanning tunnelling microscopy (STM). Furthermore, defects in graphitic network modify the electronic state of carbon that influences the shape of x-ray fluorescent, photoelectron, and absorption spectra measured density of states in occupied and unoccupied levels. Comparison of the experimental spectra with theoretical spectra calculated for the appropriate models allows making suggestion on configuration of defect.

In the present work we demonstrate how imperfections in the walls of carbon nanotubes could change their x-ray spectra. The arc- and CVD-produced carbon nanotubes before and purification and nitrogen-doped carbon nanotubes were probed. The structures of energetically stable atomic defects were determined from *ab initio* calculations on tube models. The kinds of nitrogen defects forming in CN_x nanotubes during the CVD synthesis were suggested from comparison of calculation results with x-ray photoelectron and x-ray absorption spectra. Argon ion bombrdment of CN_x nanotubes was foud to result in formation of atomic vacancies with nitrogen atoms at the edges.

Defects increase the reactivity of carbon nanotubes. We considered the processes of decomposition of bromine molecules at vacancies and topological defects and investigated a path of lithium ion penetration inside of nitrogen-doped carbon nanotubes.

MODELING OF ELECTROMAGNETIC PROPERTIES OF OLC-BASED COMPOSITES

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Electromagnetic wave absorption technology is important for a wide variety of applications. Onion-like carbons (OLC) obtained by thermal transformation of nanodiamonds are agglomerates of multi-shell fullerenes, often covered by an external graphitic mantle. Recently it was established that OLC embedded in polymer host will be ideal materials for electromagnetic absorption. At the same time onions-like carbons afford to vary composite properties owing to specific and adjustable electric properties. The purpose of these studies is to determine OLC static polarizability dependence on their structure and to investigate the static dielectric properties of a composite medium made of carbon nanostructers embedded in a dielectric matrix in thin-film geometry.

Investigation of the effect of defects on the fullerene shell polarizability was done using the semiempirical MNDO Hamiltonian within the MOPAC package. It was found that effect of topological defects on the static polarizability comes to fullerene spread radius alteration. MNDO calculations on two- and three-shell fullerene onion revealed the screening coefficient of the inner shell by the outer one is ~0.4. We proposed simple electrostatic approach to determine the polarizability of OLC which is in good agreement with quantum-chemical calculation.

The description of agglomerates was simplified by presented of them as giant onions which have diameter around 70 nm. Using the Clausius-Mossotti equation and the electrostatic polarizability value with quantum-chemistry screening coefficient we calculated the dielectric function of carbon material. The dielectric properties of OLC-based composites follow qualitatively the predictions of Maxwell-Garnett theory. In order to include holes in the internal shells of OLC we introduced porosity of carbon agglomerates.

We found a good agreement between the experimental and theoretical values of dielectric function for composites consisted of polystyrene and OLC. It was demonstrated that suggested approach gives information not only about initial carbon agglomerate but also about primary agglomerate structure.

ELECTROMAGNETIC RESPONSE OF NANOCARBON COMPOSITES TO MICROWAVES AND TERAHERTZ

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The experimental study of the electromagnetic response of onion like carbon (OLC) and OLC-based composites, along with a detailed analysis of their constitutive parameters in microwave and terahertz frequencies has been done. The complex-valued scattering matrix elements S_{11} and S_{21} of powders of these materials have been measured with high accuracy for frequencies in 26-37 GHz by a waveguide technique. The dielectric permittivity of the samples has been extracted by minimization of an appropriate criterion function using a method well known in microwave electrodynamics.

The dielectric properties of OLC-based polymer films have been studied from 20 Hz to 1 MHz to investigate structural relaxations of the OLC-PMMA composite by varying the temperature between 240 and 520 K. A small effect of the OLC concentration on the beta transition of the OLC-PMMA composite has been observed, which indicates that the embedded OLCs do not introduce any significant frustration of the rotational degrees of freedom of the ester groups along the polymer chains. That points out to the weak OLC affinity to the host matrix. By contrast, increasing the OLC concentration has been found to have strong effects on the glass and melting temperatures.

The experimental study of spectral features of OLC-based composite materials in the terahertz frequencies up to 3 THz has been presented. The EM shielding of OLC-PMMA films demonstrates quasi-resonant behavior in the frequency range near 0.3 – 0.5 THz. The observed resonant properties depend significantly on the composite films preparation and concentration of OLC inclusions. Hence, this frequency range is found to be very useful for OLC-based composites applications since their EM response to terahertz radiation is very sensitive to the concentration and type of OLC. It is found that OLC inclusions in the polymer matrix influence sufficiently the dielectric properties opening a track for a potential of using the composite material in the THz range.

The work is supported by INTAS 06-1000013-9225, NATO CBP.NR.SFPP-981051, and BRFFI 08P-019.

BANDGAP “BLUE” SHIFT OF SINGLE-WALL NANOTUBES GROWN BY ARC-DISCHARGE FROM C:BN MIXTURES

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The nanotubes with a variable bandgap are extremely desired for many applications: nonlinear optics, nanoelectronics, composite materials. Complicated post-growth procedures of the nanotube sorting and separation can be avoided in case of selective synthesis of nanotubes with the bandgap determined by the growth conditions.

In our work single-wall nanotubes were synthesized by arc-discharge method. The hollow graphitic anode was filled with a mixture of catalyst (Ni:Y_2O_3), graphite and hexagonal boron nitride *(h-BN)* powder. The BN content in the mixture was varied from 0% to 50%. For all samples (irrespective to BN content) HRTEM has revealed a presence of single-wall nanotubes.

Typical features of carbon SWNTs were observed in Raman spectra of nanotubes grown with all BN contents (0-50 %). No significant changes in G-mode (at 1592 cm^{-1}) have been detected. In a low-frequency range a position of the dominating Raman breathing mode showed a “blue shift” while BN content in the initial mixture increased. This nay be interpreted as an indirect of the bandgap increase in C:BN nanotubes.

Direct measurements of the absorption spectra of hetero-tubes were performed for the suspensions of NTs in 1%SDBS/ D_2O. The main absorption bands E_{11}^{sem}, E_{22}^{sem}, E_{11}^{met}… were blue shifted while the BN content increased in the initial mixture (Fig.1).

In conclusion, both the resonant Raman and the absorption spectroscopy have revealed a blue shift of the bandgap in single-wall nanotubes grown from C:BN mixtures. This shift has been ascribed to two effects. First, the diameter decrease led to the bandgap increase. Second, an incorporation of B and N atoms or BN clusters into the graphitic lattice of the nanotube wall led to an enlargement of the bandgap value.

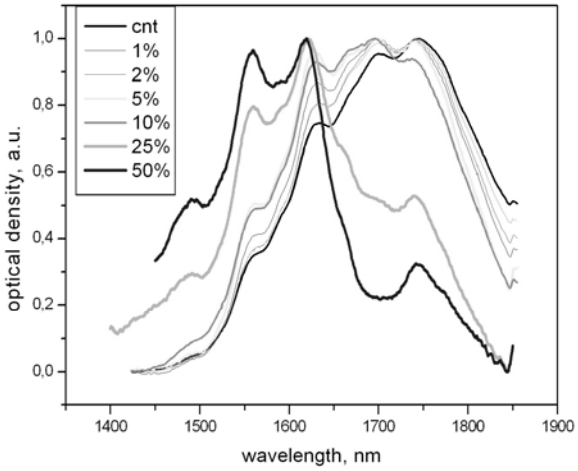

***Fig.1.** Transformation of E_{11}^{sem} optical absorption band depending of BN content in the initial C:BN mixture for arc discharge synthesis.*

This work was supported by INTAS YS 06-1000014-6355, INTAS- 05-1000008-7871 and FP6- N 033350.

Poster session I

DENSITY GRADIENT ULTRACENTRIFUGATION OF ARC SINGLE-WALL CARBON NANOTUBES

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A great breakthrough in separation of single-wall carbon nanotubes (SWNTs) has been achieved last year with application of a density gradient ultracentrifugation technique [1]. The fractions of “metallic” and “semiconducting” SWNTs have been separated [2]. This method allows also to separate nanotubes over diameter and to get the fractions showing the desired positions of the bands in UV-VIS-NIR absorption spectrum. Such narrow fractions can significantly increase the efficiency of nanotube-based ultrafast beam modulators [3,4]. Arc SWNTs demonstrate a saturable absorption in a wide spectral range 1.3-1.95 μm.

In this work the density gradient ultracentrifugation has been developed and optimized for separation of 2 types of SWNTs (HiPCO and arc). The aqueous suspensions of arc and HipCO nanotubes have been used as a starting material. Different combinations and concentrations of surfactants (sodium dodecyl sulphate (SDS) and sodium cholate (SC) were used for the gradient and reference layer formation. The spectroscopic studies (with UV-VIS-NIR optical absorption and Raman techniques) have revealed the fractions with a prevalence of metallic or semiconductor SWNTs.

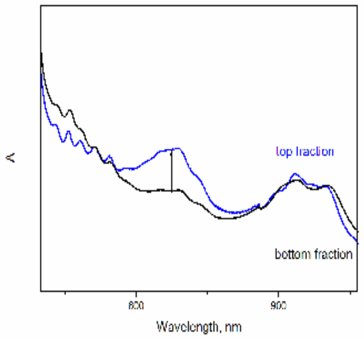

Fig.1 *UV-VIS-NIR absorption spectra of the individual nanotube fractions selected from the layers at different height. The blue color spectrum corresponds to the “metallic” fraction. The black color fraction has almost no metallic SWNT.*

The work was supported by RAS Program “Femtosecond optics and new optical materials” and FP6-033350.

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THERMOGRAVIMETRIC ANALYSIS OF NANOCARBON FILMS

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TG measurements of nanocarbon films deposited on silicon substrate by CVD were performed in static air atmosphere with heating rate 10 K/min. 3-step TG curve was obtained, demonstrating presence of three different carbon phases in the film. To study the origin of each step the CVD film was divided on a few samples. Each of the samples has been treated by heating at certain temperature from the range under consideration. After that the samples were characterized by Raman spectroscopy and by SEM. Analysis of yielded results shows that studied objects consist of nanographite flakes, diamond inclusions and some intermediate layer, which is probably the mixture of nanodiamond and amorphous carbon. These components are responsible for second, third and first steps of degradation process respectively. SEM images taken for the samples heated with different temperatures show consequent developing of nanographite flakes etching which resulted finally in formation of hexagonal holes (see Fig. 1).

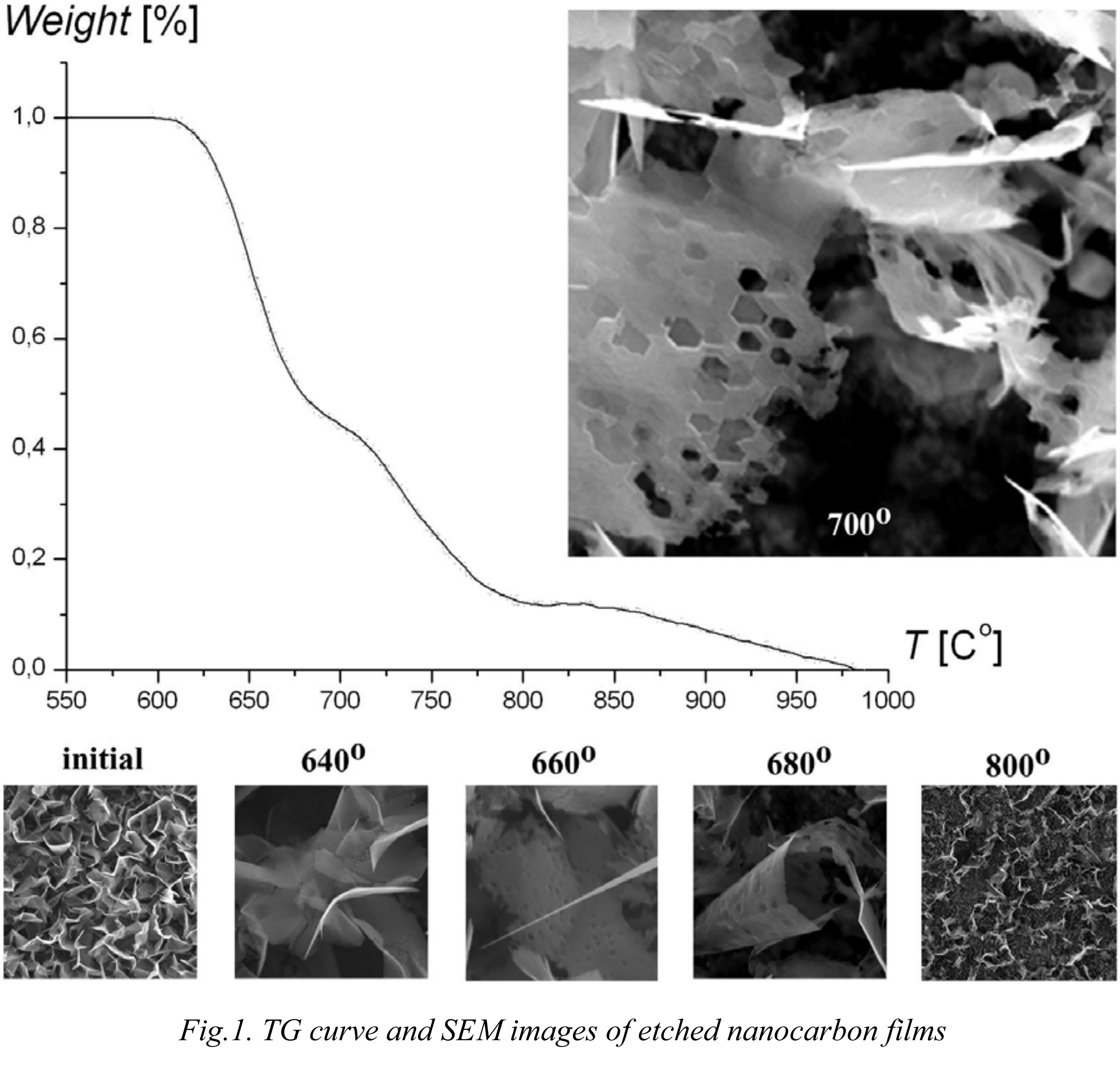

Fig.1. TG curve and SEM images of etched nanocarbon films

PLASMA CVD CHARACTERIZATION OF NANOCARBON FILM GROWTH

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We report on the characterization of direct current discharge plasma-enhanced chemical vapour deposition of nanocarbon film materials in a hydrogen-methane gas mixture. The optical emission spectra were obtained for different hydrogen-methane mixture pressures (10-150 Torr) and for different methane concentrations (0 –25%). The measurements were taken in the range of 250 – 750 nm wavelength (Fig. 1). By varying the parameters we obtain various carbon thin-film materials, the structure and composition of which are characterized qualitatively by Raman spectroscopy and electron microscopy.

The data obtained by optical emission spectroscopy show the presence of H, H_2, CH and C_2 activated species in the discharge plasma. By performing spectral measurements in different areas of the plasma we have found that intensities of hydrogen-related optical emission spectral lines are nearly independent of position, whereas intensities of optical emission spectral lines associated with CH and C_2 are significantly higher near the substrate surface than in discharge periphery areas. The presence of C_2 is particularly important in explaining the nano-graphite material formation on substrate.

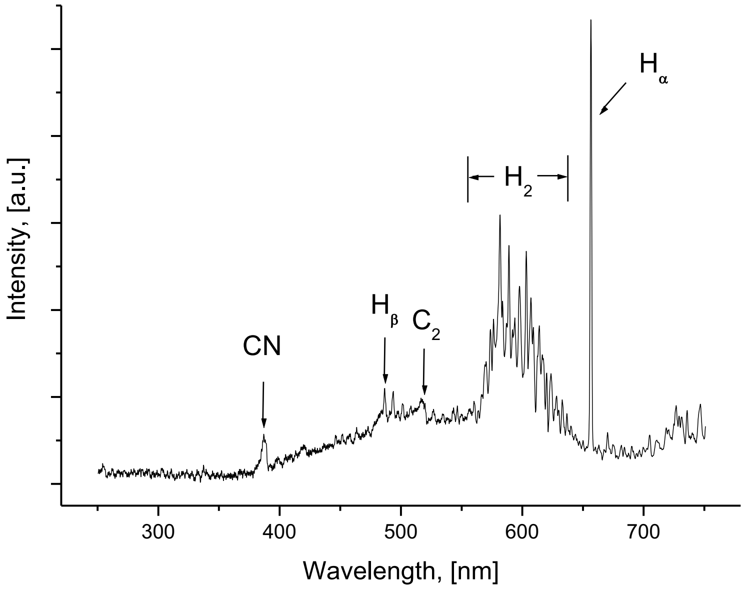

Figure 1. Typical emission spectra for hydrogen-methane gas mixture.

Raman scattering characterization of CVD graphite films

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Abstract

Raman spectroscopic study has been performed for thin graphite films grown on nickel substrates by chemical vapor deposition from a mixture of hydrogen and methane activated by a direct current discharge. Depending on the growth conditions, the CVD films are composed of graphene layers parallel to the substrate surface or of plate-like crystallites with the predominant orientation of their graphene layers perpendicular to the substrate surface (Fig.1.). A comparison of the Raman spectra for the CVD films and for the highly oriented pyrolytic graphite has been performed (Fig.2.). The mechanisms governing the Raman scattering process in the films are discussed. An important role of a double resonance mechanism in the Raman spectra of these graphite-based materials has been revealed. The Raman band positions and intensities and their dependence on excitation wavelength confirm a high degree of the structural order in the CVD graphite films.

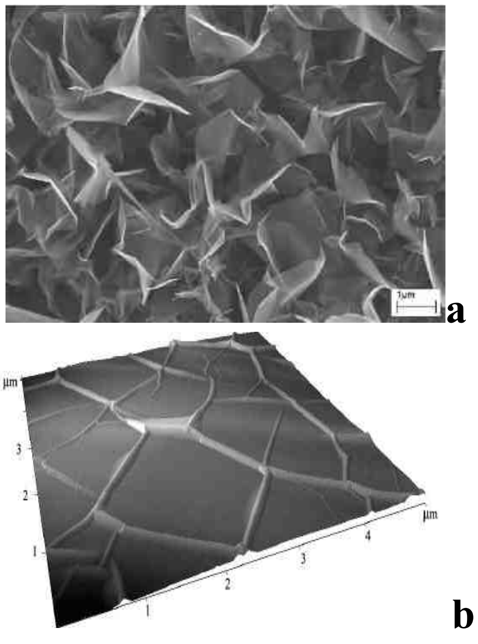

Fig. 1. The typical SEM image of the CVD nanographite film grown on Ni substrate during 60 min (a) and the typical AFM image of the CVD film obtained on nickel substrate with deposition time of 5 min (b).

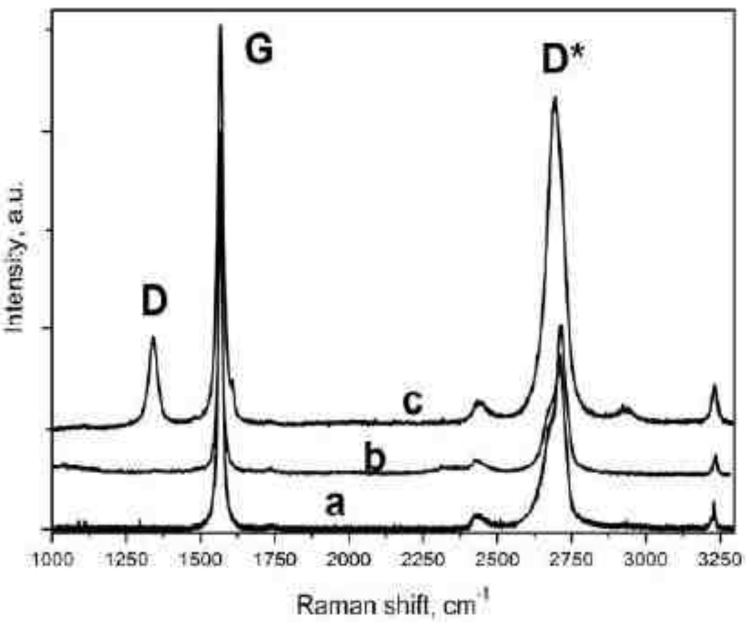

Fig. 2. The Raman spectra of the HOPG sample (a), the CVD films grown on Ni substrate during 5 min (b) and 60 min (c). The intensities in all spectra have been normalized to the G peak value. The backgrounds of the spectra b and c have a constant shift in vertical direction equal of 20% and 40% of the G peak intensity, correspondingly

FORMATION and IDENTIFICATION of GRAPHENE

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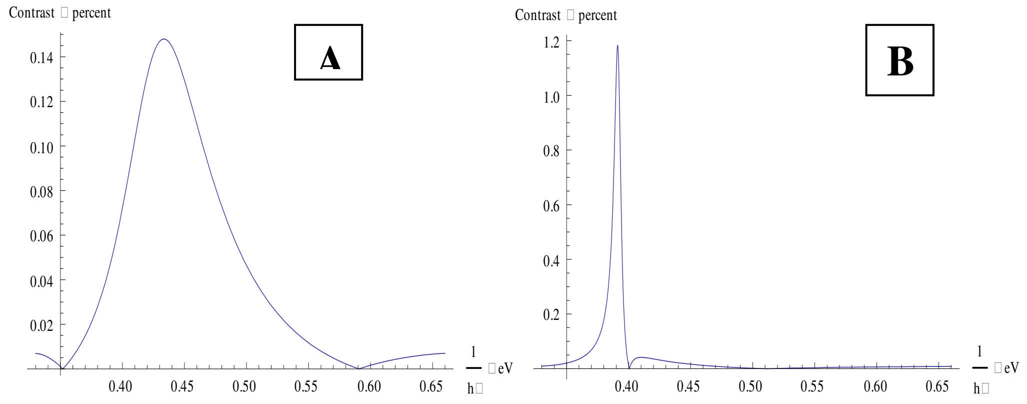
Graphene is an ideal two-dimensional carbon nanomaterial. A simple way of its preparation has been proposed 4 years ago [1]. We have learned from the authors their method of getting a single layer of graphene. Identification of flakes is necessary, but it is a 3-stage complicated task. First, an optical microscopy is the most convenient technique, but a single layer of carbon atoms is transparent. Second, an atomic force microscopy provides more exact information, but it needs a lot of time. Third, a Raman spectroscopy is a very efficient method for identification of the flakes containing 1-6 graphene layers. We propose to reduce this procedure to only one stage, that will be the easiest and the most informational. It will provide also a visibility of flakes for Raman measurements.

Quality of the optical images of carbon flakes can be described in terms of an optical contrast. A magnitude of this contrast can be defined quantitatively. This was done before, using the formulas of reflection from multilayer structures. But after calculations we also found, that a magnitude of the optical contrast depends significantly on a refractive index of the central layer (positioned between the substrate and the flake). If one would be able to make it from the material with special optical properties: the contrast of 100% and higher could be achieved (comparing with the standard value -15-20% in case of using SiO_2). In this case, it is not necessary to use any optical filters or expensive optical microscopes to allocate the monolayer carbon flakes.

The picture below shows the contrast magnitude in the standard case (carbon flake on the 170 nm-SiO_2 central layer, A), and the picture with an improved central layer (carbon flake on the layer with n=2.3, B).



The work was supported by RFBR-07-02-01505 and RAS programs.

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ARC-DISCHARGE SYNTHESIS OF SINGLE-WALLED NANOTUBES FROM C:BN:B_4C CATALYTIC MIXTURE

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For practical applications the nanotube material with a controllable band gap is required. Heterophase single-walled BNC nanotubes are predicted to have this ability. In this paper we present our work on obtaining such a material by arc-discharge method.

Several synthesis approaches had been used already to obtain BNC nanotubes. In the first approach the hexagonal BN was introduced already in the catalytic mixture C:Ni:Y_2O_3. Therefore the standard method for carbon SWNTs synthesis by arc-discharge in helium atmosphere was modified by admixture of h-BN into the anode filling. The resulting material has shown a small “blue” shift of E11 absorption band comparing with the standard material [1]. This may be considered as an indirect confirmation of integration of small BN amount (less than 1%) into the carbon nanotube lattice.

For the second approach the idea was to obtain nitrogen atoms from ambient atmosphere in the synthesis chamber, and boron atoms from the catalytic mixture. A first step for realization of this approach was a successful arc-synthesis of carbon SWNTs in nitrogen atmosphere [2]. In the subsequent experiment the boron was added as a precursor into the catalytic mixture, but none carbon nanotubes have been detected in the resulting material. One of the reasons of this fail could be a lack of boron due to efficient oxidation. Therefore, the material with a higher boron/carbon ratio could be more efficient as a precursor. From this point of view B_4C was one of the most appropriate materials.

Two sets of experiments has been performed. In all of them C:BN:B_4C weight ratio kept constant. In the first set helium atmosphere at pressure of 420 Torr has been used and the arc current varied from 75A to 105A. In the second set the nitrogen atmosphere at pressure of 350 Torr has been used and the arc current varied from 55A to 85A. The materials synthesized has been characterized in detail by Raman and UV-VIS-NIR optical absorption techniques.

The work was supported by FP6-03335 and INTAS 05-1000008-7871.

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FIELD ELECTRON EMISSION FROM NANODIAMOND

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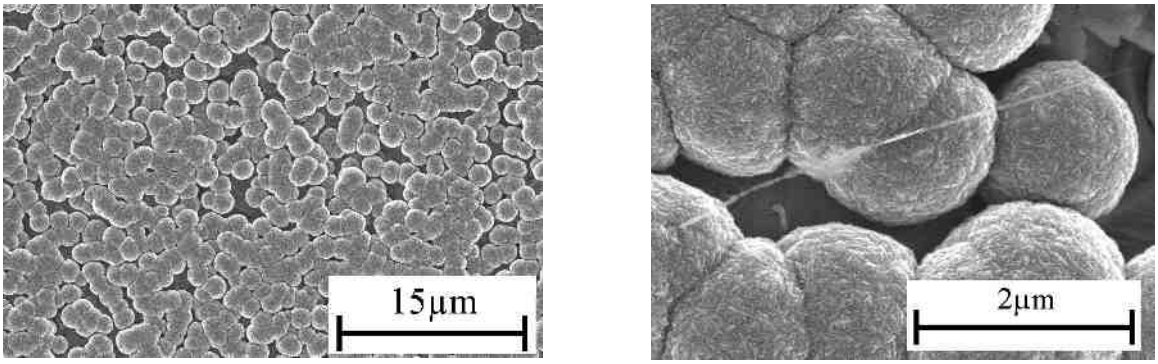
A number of experimental works demonstrate ability of nano-diamond film material produce electrons due to field emission (FE). It is believed that FE in nano-diamond occurs due to combination of negative electron affinity (which is an essential property of pure diamond surface) and reasonable electrical conductivity (resulted of non-diamond carbon material located on intergrain faces). However this approach contradicts to experimental observations were density of emission sites for nano-diamond films usually is in range of 10^2-10^4 cm^{-2}, that is more than 5 orders less than density of in the intergrain faces.

In this work we perform comparative study of nano-diamond films obtained by chemical vapor deposition (CVD) to evaluate dependence of FE property from the CVD film characteristics. The films were obtained on Si substrates and examined by scanning electron microscopy (SEM) and Raman spectroscopy (RS). The FE characteristics were obtained in flat vacuum diode configuration with use of phosphor coated anode screen.

We found that the nano-diamond CVD films having very similar surface morphology (Fig1. a) and material composition may be very different in electron emission. Our careful investigation shown that the films exhibiting the most efficient electron emission (i.e. higher emission site density and density of averaged emission current) contain on their surface tip-like elongated carbon structures (Fig1. b). The density of these type of structures on the film surface coincides with the FE site density. However by having so small density these structures cannot be detected with RS and thus their composition is not clear. Also these structures are not available for analysis till now by such techniques as high resolution transient electron microscopy. Nevertheless good agreement with the density of the FE sites allows us to suppose that these carbon structures are responsible for the observed electron emission.



a **b**

Fig. 1. (a) typical SEM image of nano-diamond CVD film, (b) detailed view of nano-diamond CVD film with good emission properties.

FABRICATION OF TRANSPARENT THIN FILMS FROM POLYMER/SINGLE-WALL CARBON NANOTUBES COMPOSITE FOR OPTOELECTRONICS

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Carbon nanotubes are a nanosized material with unique physicochemical and physical mechanical properties. During last years the investigations of transparent thin films from polymer/single-wall carbon nanotubes (SWNT) composite aimed mostly fabrication of optical material with a high non-linearity for optoelectronics.

We are developing strategie of chemical modification of the SWNT based on the noncovalent interaction of the nanotube surface with different chemical reagents. In the report, we present the results of studying the noncovalent interaction of SWNT with amphiphilic reagents (surfactants, calixarenes) and different polymers [1,2]. The chemical modification of SWNT made it possible to obtain the nanocomposite materials based on nanotubes with specified properties that can be involved in subsequent nanotechnological processing. A complex of methods (FTIR, UV-VIS-NIR optical absorption, Raman scattering techniques, AFM and conductivity measurement) was used to prove the chemical addition of functional groups to the nanotube and to study the properties of the obtained nanomaterials.

The studies performed made it possible to develop the nanocomposite optical materials based on SWNT (HiPco and arc discharge) and water-soluble polymers (polyvinyl alcohol and carboxymethylcellulose). These are films of specified thickness (5–100 μm) optically transparent in the 300–2000 nm interval, which are promising for practical use as principally new nonlinear optical media for application as ultra-fast (picosecond and subpicosecond) stable modulators of light flows in laser physics [3,4].

This work was financially supported by the RFBR 08-03-01017a

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COMPUTER MODELING OF FIELD EMISSION FROM NANOCARBONS

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Effective field emission from various nanocarbon materials makes them very efficient electron sources which can be used as cold cathodes for vacuum microelectronic devices. Study of the field emission phenomena can provide an important information about the fundamental properties of materials. The field emission properties of nanocarbon materials depend on their topology and electronic structure. Experimental study of these properties often indicates an inconsistency between experimental results and present theory of the field emission from nanocarbons.

In present work we introduce several models which can provide an explanation for some experimental features of the field emission from nanocarbons. We have performed the computer simulations based on Fowler-Nordheim theory for various types of nanocarbons. During modeling the following aspects have been taken into account: influence of emitter shape on emission stability, screening effect for arrays of differently shaped emitters, mechanical flexibility of nanocarbons and others.

ON THE ROUTE TO BOLOMETERS BASED ON SINGLE-WALLED CARBON NANOTUBES

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The optical properties of single-walled carbon nanotubes (SWNT), including photoconductivity, suggest outstanding potential for applications in nanoscale-sized optoelectronics. In particular the large photoresponse that is observed for suspended SWNT films make them attractive candidates for the sensitive element of an infrared bolometer. Other parameters are also very promising. First, recent works [1] report a temperature coefficient of resistance of $5\%.K^{-1}$ which can be favorably compared to standard materials such as VOx or a-Si. Then the high thermal conductivity of a SWNT ($6600\ W.m^{-1}.K^{-1}$ at 300 K [2]) is a key to ensure high signal-to-noise devices working at room temperature. Eventually the flexibility of nanotubes films allows for original geometries.

The work reported here concerns the realization and characterization of SWNT films suspended between interdigited platinum electrodes. These electrodes are deposited over a silica layer on a silicon substrate with inter-electrode distances varying from 1 μm to 10 μm. We use commercial SWNT powders, purified by means of sonication and centrifugation. Aqueous solutions of such purified nanotubes are filtered on a nitrocellulose film, which is then deposited on the interdigited electrodes and eliminated by an organic solvent. The obtained devices are characterized by I-V measurements under controlled atmosphere and for temperatures varying from 100 to 300 K.

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Wednesday, August 6

Optical advanced spectroscopic techniques for the study of nano-structured materials: application to carbon nanotubes

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Nano-materials are nowadays used in various domains whenever they exhibit properties that are of interest in terms of applications. Reliable materials require pertinent characterization studies in order to insure reproducibility in their preparation. To achieve this goal, new tools have been developed, besides the well-known transmission electron microscopy and near-field microscopies (AFM or STM, ..). In particular, optical techniques have been greatly improved with the use of Raman Scattering in specific confocal conditions, Surface Enhanced Raman Scattering (SERS) and near-field optical spectroscopy (SNOM). Applied successfully to individual molecules, these non-destructive techniques have also been used to study nano-materials and exploited in-situ to investigate in details the modifications in the spectroscopic features of the studied materials when they are embedded in host matrices for example.

In this presentation, we will review the most recent developments of these new optical spectroscopies and illustrate their usefulness by describing few examples, such as the different types of functionalization encountered in carbon nanotubes and carbon nanotubes/conducting polymers nano-composites.

In addition, the SERS spectroscopy has allowed us to put in evidence a new effect: a “single-beam pumped” Coherent anti-Stokes Raman Scattering (CARS)[1]. As a matter of fact, giant optical fields are locally generated in nanoscale metal structures through the local excitation of surface plasmons and yield a variety of nonlinear optical processes. Using silver and gold, reproducible enhancements of the Raman signal of the order of 10^2 – 10^4 on various polymeric and semiconducting materials including carbon nanotubes, have been demonstrated. Furthermore, an abnormal anti-Stokes Raman emission, reminiscent of Coherent anti-Stokes Raman Scattering (CARS), is accurately observed on nanometric thin film on different materials such as carbon nanotubes. We demonstrate that under a tight–focusing of the excitation light, a CARS emission, resulting from a wave mixing process between the incident laser light (ω_l) and Stokes Raman light (ω_S) generated by a Surface Enhanced Raman Scattering (SERS) mechanism, is produced.

Abnormal anti-Stokes/Stokes intensity ratios are also observed for carbon nanotubes in powders, presumably due to CARS-type effects. These results originate from two important facts that are due to bundles: the up-shift of the radial mode frequencies on one hand and the decrease of the electronic transition energies on the other hand. We can clearly identify the state of the nanotubes, either. in an isolated form or in bundles. Moreover, it is observed that the higher the anti-Stokes/Stokes ratio anomaly, the larger the bundles.

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Application of laser-based diagnostic to *in situ* study of nanotubes synthesis

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Experimental studies were conducted during synthesis of Carbon and BN Single Wall Nanotubes (SWNT) by CO_2 laser vaporization of a rotating target.

A reactor was first developed at ONERA to produce carbon SWNT by continuous vaporisation of C:Co:Ni target in He flow using a 1500W CO_2 laser. Optical diagnostics of the hot flow have been performed using a combination of Coherent Anti-Stokes Raman Scattering (CARS), Laser Induced Fluorescence (LIF) and Laser Induced Incandescence (LII) to probe respectively the temperature, the species concentration of Ni, Co, C_2, C_3 and the soot size and density. CARS allow us to measure the vertical profile of temperature above the carbon target which is heated by the CO2 laser. LIF diagnostic reveals the evolution of metal vapour, with a peculiar behaviour appearing as a plateau due to supersaturated vapour above liquid catalyst nanoparticles (Fig. 1). The vapour density is seen to drop at about 7mm above the target as a result of complete solidification of metal-carbon clusters below 1400K. The evolution of the soot size (LII) is seen to changes from linear to non linear when metal catalysts are added to the target composition (Fig. 1a). The soot size suddenly increases at the location where metal vapour disappears thus indicating that nucleation and growth occurs (Fig. 1b). *In situ* measurements have brought new insight into the role of catalyst and hot gas composition on the condensation of carbon to form SWNT.

In the same reactor, BN nanotubes are produced from vaporization of hBN target. Atomic boron and boron oxide (BO) vapours are probed using LIF. The spatial evolution of Boron concentration is compared to the temperature profile measured by CARS and to saturated vapour pressure of boron calculated from temperature. The BN products are seen to produce an UV photoluminescence also.

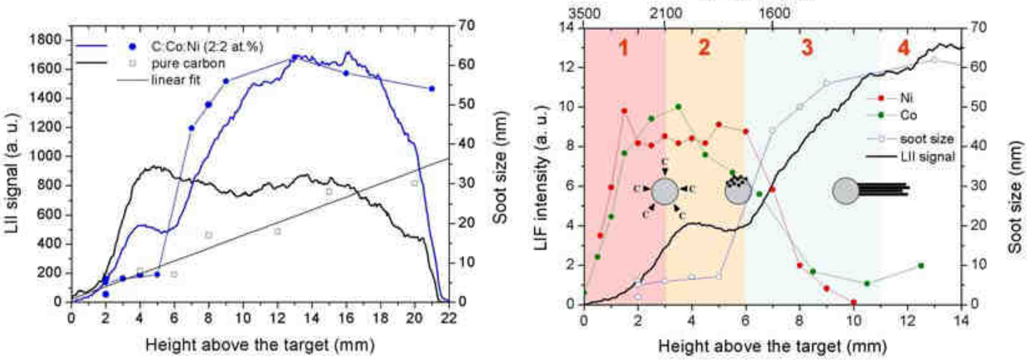

Figure 1: (a) Spatial evolutions of size and volumic fraction of soot particles in He at 300 mbar, 50 ml.s^{-1} and target temperature of 3500 K composed of C:Co:Ni (96:2:2 at.%, blue line) and pure carbon (black line). (b) Spatial evolutions of Co, Ni and soot compared to the VLS model predictions.

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Poster session II

ATOMIC FORCE MICROSCOPY AND RAMAN SPECTROSCPY OF GRAPHENE LAYERS

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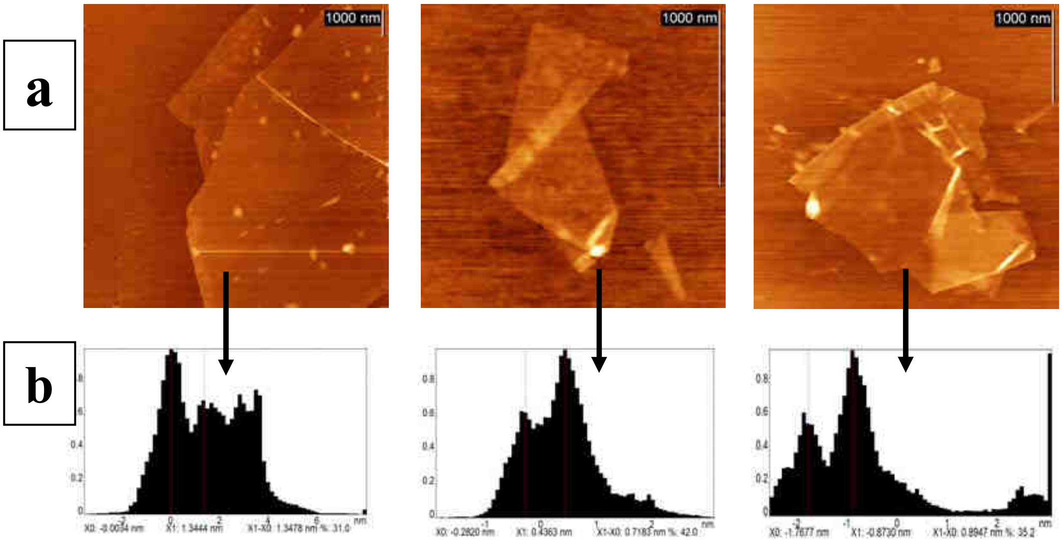
In this work the results on preparation and analysis of structural properties of the graphene layers are presented. We have applied the microchemical cleavage technique for the graphene layers preparation. The obtained samples consisted of numerous n-layers graphene flakes.

A large number of the flakes was studied by the atomic force microscopy in order to estimate the number of layers in the flakes. The typical AFM images are presented in the Fig.(a). The graphene flakes thickness distribution over the samples was histogrammed Fig.(b). The distribution exhibits a row of maxima: 0.7 nm, 1.1 nm, 1.4 nm, 1.7 nm, 2.1 nm etc. These values correspond ideally to the one-, two, three- etc layers of graphene.



The flakes characterized by AFM were studied by Raman spectroscopy for the electronic properties of the sample analysis. The electronic structure for the graphene flakes of different thickness was modeled using the density functional method [1]. The data obtained by Raman spectroscopy were used for the model accuracy analysis. A perfect correspondence between the thickness and the electronic structure was observed.

This work was supported by RFBR-07-02-01505

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OPTICAL SPECTROSCOPY OF FULLERENE-ZN(II)TETRAPHENYLPORPHYRIN COMPLEXES

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Fullerene-porphyrin complexes have been the subject of intense research as artificial systems that efficiently convert sunlight into energy and, upon a sequence of electron transfer processes, generate chemical or electrical power. [1,2]. Fullerene complexes with metalloporphyrins are natural chromophores strongly absorbing in the visible range. In this work the interaction of molecular components, as well as optical, vibrational and photoelectrical properties of C_{60}-Zn(II)tetraphenylporphyrin (ZnTPP) thin films has been investigated and *ab initio* calculations of optimized geometry, electronic structure, and vibrational properties ZnTPP-C_{60} have been carried out. The method of density functional theory with B3LYP hybrid functional was employed. It is shown that ZnTPP-C_{60} is a charge transfer complex with E_{dis}=0.6 eV. The calculated values of HOMO-LUMO gap E_{g} for the simple complex and ZnTPP-C_{60}-ZnTPP trimer are 1.38 eV and 1,73 eV correspondingly.

We have performed the UV-Vis-NIR absorption spectroscopy studies and Raman scattering investigations of complex fullerene Zn(II) tetraphenylporphyrin thin films produced by vacuum evaporation in hot-wall reactor. Hot wall techniques allows the growth of epitaxial layers close to thermodynamic equilibrium, which is essential in the case of van der Waals molecular system and increase the possibility of self-organization process under the complex formation. It is shown that an additional absorption band at 1.38 -1.53 eV which corresponds to the calculated value HOMO-LUMO gap of C_{60}-ZnTPP complex, appears only in complex films grown at certain technological conditions. The Raman spectra provide evidence for the complex formation through the appearance of the A_{g2}-derived modes at 1460 and 1452 cm^{-1} which manifest the charge transfer in the complex.

Photoluminescence of both ZnTPP and C_{60}-ZnTPP films and time dependence of main peaks are measured. The formation of the charge-transfer complex leads to the quenching of the photoluminescence in the region of ZnTPP lighting (620 nm) and to the increase of luminescence intensity in the region peculiar to C_{60} (750 nm), as well as to the changes in fluorescence kinetics.

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CONFINEMENT OF OPTICAL LIMITING OF ONION-LIKE CARBON BY LASER INDUCED OPTICAL BLEACHING IN N,N-DIMETHYLFORMAMIDE.

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Onion-like carbon (OLC) produced via annealing of explosive nanodiamond (ND) are perspective for the development of optical limiting materials [1]. Here we have studied the interaction of laser irradiation (λ=1064 nm) with OLC suspension in *N*,*N*-dimethylformamide. The suspensions of OLC sample were previously characterized by PCS to estimate size of aggregates, TEM and UV-Vis spectroscopy. It has been found that the OLC structures exhibit strong optical limiting action if one use defocused laser irradiation while usage of focused laser radiation results in the optical bleaching of OLC suspension. Thus at high power laser irradiation the effect of bleaching overcomes the optical limiting of OLC. The results are discussed in terms of photoinduced electron transfer reaction of curved OLC shells with H-donor DMF molecules. This reaction can be used for surface functionalization of OLC.

Acknowledgements: The work was partially supported by the NATO Science for Peace program (grant SfP-981051), INTAS (grant 06-1000013-9225) and by the Ministry of Science and Technology of the Russian Federation (project no. RNP.2.1.1.1604)

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TiO_2 PARTICLES IRRADIATED BY UV LIGHT: FORMATION OF FREE RADICALS

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Skin protects deeper located organs from various hazards of the environment, mechanical, chemical, optical etc., in particular, from UV light. Exceeding doses of UV radiation can cause direct or indirect (via formation of free radicals) DNA damage leading to carcinogenesis. Titanium dioxide (TiO_2) nanoparticles are extensively used nowadays in cosmetics, paints, air and water waste purification. Between three existing crystal modifications of TiO_2 (anatase, rutile and brookite), anatase is the most photoactive if irradiated by UV light. It is reported that both anatase and rutile particles used in sunscreens oxidise DNA and RNA *in vitro* and in human cell culture under UV irradiation. However, it is important to know, if the amount of radicals generated by the particles on skin exceeds that of produced by skin itself.

Free radicals are molecular species with an unpaired electron on external orbital and of high chemical reactivity. Under normal conditions the amount of free radicals produced in organism, is balanced by enzymes and antioxidants. An excessive increase in radical production is involved for example in the pathogenesis of cancer, diabetes mellitus etc. The alien free radicals appear as a consequence of effect of ionizing radiation, UV light, xenobiotics etc. and are harmful.

In this paper, we prove experimentally by means of the EPR (electron paramagnetic resonance) spectroscopy, the small (25 nm in diameter) nanoparticles of titanium dioxide (anatase form) are more photoactive than the large (400 nm in diameter) particles. This effect is clearly seen if particles embedded in placebo are applied on glass and it is in agreement with the Mie theory. However, if applied on porcine skin, no distinct difference is observed. This is caused by large skin contribution to generation of radicals. In comparison to skin ability to produce radicals, the nanoparticles do not play significant role at used concentrations (2 mg cm^{-2}).

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GLUCOSE EFFECT ON THE DIFFUSE REFLECTANCE OF FEMTOSECOND LASER PULSES FROM BIOTISSUE PHANTOMS

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Noninvasive and continuous monitoring of glucose concentration in human blood and tissues is one of the most challenging and perspective problem of optical biomedical diagnostics. The major difficulty in development and clinical application of optical methods of noninvasive glucose sensing is associated with relatively low changes of biotissue optical properties caused by glucose. This results in quite low sensitivity of these methods and demands high accuracy of measuring devices to overcome the difficulty.

It is known that the variation in glucose concentration in biotissue affects its light scattering parameters: refractive index, scattering crossection and phase function, as well as anisotropy. Thus laser pulse propagation through tissue should depend on glucose concentration. Our study aims to assess the effect of glucose on the diffuse scattering of ultrashort laser pulses from single layer and three layer physical models (phantoms) mimicking human skin.

A set up was built on the basis of a streak-camera with 10 ps temporal resolution and a Ti:Sapphire laser with central wavelength 800 nm, pulse duration 40 fs, repetition rate - 10 Hz, and energy - up to 40 mJ. This set up allows us to detect with temporal and spatial resolution the radiation diffuse scattered from the studied medium. Probing pulses were delivered with similar optical fibers with core diameter of 300 μm to the studied phantom and directly to the streak-camera to serve as a reference. The pulses diffuse backscattered from the phantom were collected by 10 adjacent optical fibers placed one by one at different source-detector separations from 0.53 to 5.3 mm and delivered to the streak-camera. After averaging over 25-30 pulses, the peak intensity, total energy and temporal profile of the signal from each detecting fiber were calculated. We obtained the relative sensitivity of the above parameters to the variation of glucose levels in the concentration range from 0 to 1000 mg/dl at different source-detector separations. In the case of the single layer phantom made of 2% aqueous solution of lypofundin, the peak intensity of the scattered pulse appeared to be the most sensitive parameter. The relative sensitivity for this parameter is 0.027 % / [mg/dl]. In case of the three layer phantom (a layer of blood with the hematocrit equal to 35 % was placed between two layers of lypofundin 2 %), the peak intensity and the total energy of the detected pulses have practically equal sensitivities which depend on the source-detector separation. In this case, the relative sensitivities are up to 0.030 % / [mg/dl].

This work was partially supported by RFBR grant № 06-02-17015-a, RFBR-Academy of Finland grant № 08-02-91760. A.V. Bykov also acknowledges the support of GETA Graduate School, Infotech Oulu and Tauno Tönning foundation.

Optical scheme for measurement of Raman scattering from small objects.

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The optical scheme of Raman scattering measurements from small objects for investigation of structural defects was realized with high spatial selectivity. High-accuracy spatial focusing of stimulating light on the sample was reached with using of microscope objective instead of focusing lens. There were commit measuring of spatial selectivity with different magnification objectives. Depth selectivity of Raman scattering intensity was measuring in dependence from silicon plate deviation from focal plane of microscope objective. Planar selectivity was estimated from width of entrance slit that takes all collected light. Intensity was measured from silicon stokes Raman spectra. The best result was 30 µm “in depth” and 11 µm of “planar” selectivity.

TRANSIENT CONDUCTIVITY IN DIAMOND INDUCED BY SHORT AND ULTRASHORT LASER PULSES IN THE SPECTRAL RANGE FROM IR TO UV.

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Diamond is often considered as an ideal material for electronic devices employing free electrons and holes induced by ultra-short laser pulses. The wide band gap, outstanding resistance to exposures by high energy quanta make it especially attractive for diagnostics of this kind of radiation, while its electron structure enriched by intrinsic and impurity defects provides interesting photo-conductive properties in the IR-UV range. Characterization of diamond is still not complete in many aspects including mechanisms of free charge relaxation, trapping of charge and nonlinear optical properties. Using of optical harmonics of Ti:Sa laser (1.5÷6.2 eV), a dye laser operating at 654 nm and an OPO, tunable through the visible range, in combination with a technique of transient photoconductivity (TPC) [1], allowed to fill some of the gaps mentioned.

TPC method employs fast measurements of a transient current in the exposed area of the crystal. The shape, the peak voltage and intensity dependences of TPC signal allow to estimate concentration of free charges, to reveal mechanism of their generation and the following space charge formation, to measure lifetime of drifting electron and holes, within the bandwidth of a fast oscilloscope.

TPC in the visible and near UV range was explored in more details, which allowed to reveal an enhancement of photocurrent related to trapping of electrons on residual defects of some sort. TPC signals in the visible range increased up to 10 times after exposure of the crystals to UV pulsed or CV radiation [2]. The initial conductivity level could be then retrieved by annealing in air. Results of photoconductivity experiments were compared to photoemission data obtained in similar conditions. To identify the traps, complementary information was obtained by means of EPR spectroscopy. It was found that the most likely defect, introducing such an enhancement, was combination of a vacancy and an interstitial nitrogen ion. To vary concentration of these deep traps in the material, diamond samples were exposed to electron beams.

The results of the research allow to monitor trapping dynamics, to recognize trapping centers and to reveal their role in space charge formation processes. Exposure of diamond to high energy electron beams and to low intense UV light was shown to effect photoconductive properties of the material, which can be used either for fine trimming of diamond based photoelectron devices or for development of elements with variable (adjustable) sensitivity.

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LASER ETCHING OF UNCD FILMS

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Recent scientific advancement in the production of nanocarbon-based materials, such as fullerenes, nanotubes and ultrananocrystalline diamond (UNCD) established the potential for nanofabrication technology. UNCD films properties and also methods of cleaning, treatment and structure modification have been widely discussed in literature [1, 2]. Laser treatment may become one of the powerful instruments for UNCD films structure modification.

This work investigates excimer laser action (λ=248 and 193 nm, τ=20 ns) on the UNCD films with different N_2 doping levels (0% and 30%). The UNCD films were deposited on polished Si substrate in a microwave plasma CVD reactor (DF-100 model, 5 kW, 2.45 GHz) in $Ar/CH_4/H_2/N_2$ mixtures. The thickness of deposited films was 2 microns. The UNCD films was analysed with Raman spectroscopy, interference microscopy (New View 5000, Zygo Corp.) and scanning electron microscopy (SEM, QUANTA) in low vacuum.

The ablation rate of UNCD films of both types was found to be strongly dependent on laser fluence and is characterized by the presence of threshold. Thus ablation with typical rate over 10 nm/pulse dominates at laser fluence above 1 J/cm^2. Otherwise, at fluence below 1 J/cm^2 etching rate is three orders of magnitude lower. Also it should be mentioned that the etching rate of doped films is drastically higher than non-doped one, which is explained by high absorption in UV region. It is a well-known fact that N_2 doping level increase leads to increase of sp^2 phase [3] which influence absorption. It was shown that laser etching technique combined with conventional surface analyzing methods can be efficient tool for bulk structure investigation. With this complex technique nonlinear dependence of the crater depth from the number of pulses was found at low laser fluence. Investigation of this phenomenon will be presented and discussed.

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ELECTRONIC STRUCTURE OF THE VAPORIZED BN-NANOMATERIAL PROBED BY OPTICAL ABSORPTION AND X-RAY SPECTROSCOPY

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The electronic structure of BN-nanomaterial, obtained by laser vaporization of BN target under a nitrogen atmosphere, has been investigated using optical absorption and X-ray spectroscopy. Transmission electron microscopy and X-ray diffraction showed that the sample mainly contains single-wall BN-nanotubes, boron particles encapsulated in a few-layer BN-shells, BN-cage and boron oxide.

The optical absorption spectrum of BN-nanomaterial was recorded on a Shimadzu 3101 PC instrument in a range of 0.4-6.5 eV. Three bands located at 6.2, 5.4 and 4.45 eV were recognized in the spectrum. The first band corresponds to the optical gap of BN-nanostructures, the origin of the other bands is under investigation.

X-ray emission (XES) and absorption near-edge spectra (XANES) of BN-nanomaterial, as well as reference samples of hexagonal boron nitride, boron oxide and amorphous boron were measured. The B K_α XES spectra were recorded with a laboratory spectrometer, where a single crystal of ethylene glycol distearate was used as an analyzing crystal. The B1s and N 1s XANES experiments were performed at BESSY-II storage ring (Berlin) on the Russian-German synchrotron radiation beamline. The B K_α XES spectrum of BN-nanomaterial was decomposed into the B K_α XES spectra of components occurred in the BN-nanomaterial. From this decomposition a component’s ratio in the sample was estimated. It was found that the vaporization method produced about 5% of BN nanostructures.

Results of *ab initio* calculations of the electronic structure of BN-sheet and BN-tube (B3LYP method, 6-31G* basis set) were carried out to interpret the experimental x-ray spectroscopy data. The theoretical B K_α XES spectra of BN-sheet and BN-tube were constructed using the results of quantum-chemical calculations. Comparison between the theoretical B K_α spectra of BN-sheet and BN-tube demonstrated the insignificant difference in the electronic structure of these objects.

Information about unoccupied states of boron and nitrogen in BN-nanomaterial was obtained from the B 1s and N 1s XANES spectra.

NANOSECOND PHOTON DRAG AND OPTICAL RECTIFICATION EFFECTS IN CARBON NANOSTRUCTURES

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Intense laser pulses can produce quasi-static electric field due to photon drag (PD) and optical rectification (OR) effects [1,2], which manifest themselves as a dc current due to transfer of the photon momentum to free carriers, and a dc polarization, respectively. In isotropic media, these nonlinear optical phenomena result in the generation of a current density $j(t)$ along the incident wave vector, $j(t) = C_{PD}I + C_{OR}\frac{dI}{dt}$, where $I(t)$ is the light intensity, C_{PD} and C_{OR} are relevant material parameters. We report a theory of the dc response of the 2D (nanographite film) and 1D (CNT yarns) nanocarbon (nC) materials irradiated by nanosecond laser pulses. We interpret results of recent experiments [3, 4] and demonstrate that PD dominates the dc response in nC materials.

A voltage appeared across the irradiated nC samples, proportional to the power of the light beam and depends on its spatial profile. The potential Φ of the quasi-static electric field $\mathbf{E} = -\nabla\Phi$ in the film is described by the following equation: $\nabla^2\epsilon\Phi = -\frac{\epsilon}{\sigma}\cdot\frac{\partial}{\partial x}\cdot\left[C_{PD}.I(t) + C_{OR}.\frac{dI(t)}{dt}\right]$ Where x is along the beam, σ is the conductivity, ϵ is the permittivity of the film. The light-induced charge separation gives a dipole-like nature to the electric field (see Fig.1).

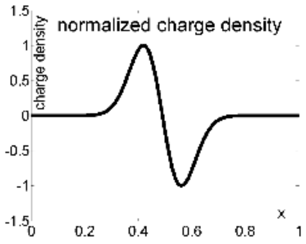

Fig.1. the light-induced electric charge density's profile along the longitudinal axis of the film.

In both 1D and 2D nC materials, the temporal profile of the generated electric signal nearly coincides with the shape of the incident light pulse. This indicates that PD dominates the dc response. Our numerical simulation shows that in these nC materials, under wavelength $1\mu m$, $C_{PD} = 1,5 \times 10^{-3} A/W$, i.e. it is of the same order as in semiconductors (Ge, Te) and metals (Bi, Nb).

In conclusion, we developed a theory of dc response of the 2D and 1D nanocarbon materials under irradiation with nanosecond light pulses. The demonstrated strong PD effect makes nanographite films and CNTs yarns strong candidates for conversion of the pico- and femtosecond light pulses into THz radiation.

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Passive mode-locking of Nd-doped solid state lasers operated at λ=1.3 µm using carbon nanotubes as a saturable absorbers

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Development of compact lasers with a stable generation of ultrashort pulses in infrared spectral range is rather actual problem now. Thus the lasers operating at wavelength λ= 1,34 µm are especially actual now for development of fiber-optic electronics.

In this work, we demonstrate passive mode-locking of flash-lamp and diode pumped ($Nd:GdVO_4$, $Nd:Y_{0.9}Gd_{0.1}VO_4$ and Yag:Nd respectively) solid state lasers [1] operated at 1.3 µm wavelength using a novel saturable absorber consisted of single-wall carbon nanotubes (SWNT) incorporated in a polymer matrix [2-4]. One of the most attractive properties of these SWNT-based saturable absorbers is an opportunity to control the absorption spectrum of the film by choosing SWNTs with necessary diameter distribution. In addition the SWNT-based absorbers have sub-picosecond relaxation time of electronic excitations and high laser-radiation endurance.

We employed SWNTs created by a high pressure CO-gas decomposition (HiPCO) synthesis technique. One can observe from Fig.1 that the laser wavelength (1.34 µm) almost coincides with the center (1.314 µm) of the sharp absorption band of the semiconducting nanotubes with diameters of 1.1 nm [5,6].

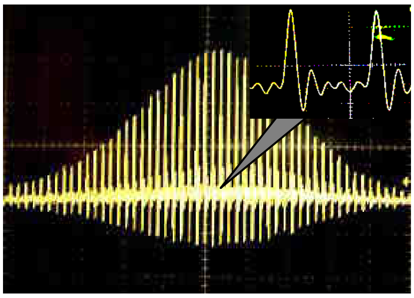

Fig. 2. The Generation oscillogram of $Nd:Y_{0,9}Gd_{0,1}VO_4$ laser operating in a self mode-locking regime with a “polymer+SWNTs” film inserted in resonator

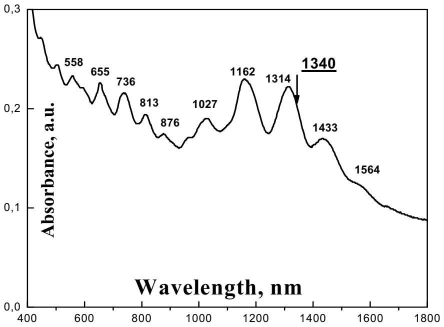

Fig.1. The optical absorption spectrum of a free-standing carboxymetylcellulose film incorporating HiPCO single-wall carbon nanotubes in a spectral range 400-1800 nm. The operation wavelength of $Nd:GdVO_4$ and $Nd:Y_{0.9}Gd_{0.1}VO_4$ lasers (1.34 µm) is shown by an arrow.

Laser pulses with the output energy up to 50 µJ and the duration of 30 ps at 1.34 µm wavelength and pulses with the output energy up to 70 µJ and the duration of 50 ps at 1.32 µm wavelength were generated.

In this work we demonstrate for the first time a self mode-locking regime with SWNT-based films as fast saturable absorbers in the solid state lasers operating at λ= 1,3 µm.

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Thursday, August 7

Carbon Nanotube Nanocomposites for Printable Flexible Displays, Solar Cells and Optical Limiters

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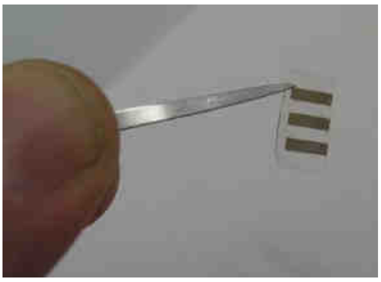
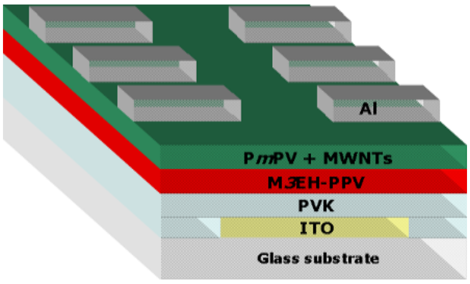
Nanostructured Materials are expected to become essential building blocks of future devices. New developments in this area will impact on a vast range of technologies ranging from electronics, chemical engineering, medical device technology to pharmaceutical and bio-technology, within the next few decades.

The controlled incorporation of nanostructures into polymers can completely alter the physical and chemical properties of the polymers. A controlled incorporation of such structures at nanoscale will yield novel multifunctional composites. Applications of such materials may, for example be found in aerospace industry (superb strength/weight ratio, microwave absorption), pharmaceutical industry (electrically and mechanically induced release of drugs) and transport sector (scratch proof, electrically conducting coatings).

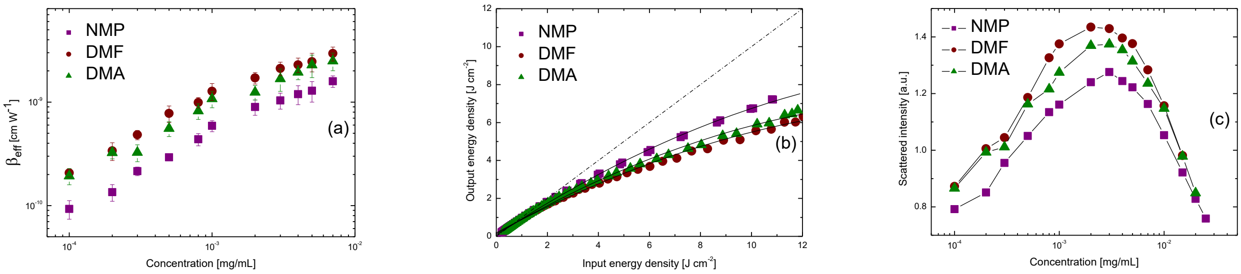
Advances in fabrication, purification and processing techniques have allowed carbon nanotubes to fulfill their great potential in many areas. Existing in two forms, multi-walled and single-walled this form of carbon has been shown, both experimentally and theoretically to have excellent mechanical and electrical properties. Individual nanotubes have elastic moduli in the region of 1 TPa, and in powder samples, bulk conductivity as high as 10^5 S/m has been measured. We have achieved solubility in selected organic solvents had have incorporated Carbon nanotubes into polymers through a unique wrapping process. In both cases, the resulting material has the potential to be used in printed electronic, photonic and sensing devices.

We believe that the most accessible applications are those using nanotubes to improve the performance of existing functional organic electronics. The effects of incorporating multi-walled carbon nanotubes (MWNT) in two existing functional organic devices: organic light emitting diodes (OLEDs) and organic solar cells have been studied. Single layer OLEDs and organic photovoltaic devices were firstly prepared and characterised in order to understand the physics of conjugated polymers based organic devices without the use of MWNT. Careful analysis of the device's characteristics of a single layer OLED allowed us to determine the intrinsic electronic parameters (Fermi energy level, majority charge carriers' mobility, …) of one the main conjugated polymers used throughout this Thesis: poly(2,5-dimethoxy-1,4-phenylenevinylene-2-methoxy-5(2'-ethylhexyloxy)-1,4-phenylenevinylene (M3EH-PPV). As regards single layer polymer solar cells, we found that only a very thin layer was photo-active, resulting in power efficiency being greater for thinner polymer solar cells. Before using it in OLEDs and organic photovoltaic devices, a poly(m-phenylene-co-2,5-dioctyloxy-p-phenylenevinylene) (PmPV) and MWNT composite (PmPV+MWNT) was prepared and characterised. Both DC and AC conductivities of the composite were measured. Percolation scaling laws were used to discuss the results, and conduction due to fluctuation induced tunnelling was indicated. Absorption and photoluminescence studies on M3EH-PPV and PmPV+MWNT bilayers revealed that energy transfer from M3EH-PPV to PmPV, followed by charge transfer from M3EH-PPV to MWNT is likely to occur. Using the PmPV+MWNT composite in M3EH-PPV based OLEDs, a potential barrier to both holes and electrons at the M3EH-PPV / composite interface was observed. However, at all nanotube to polymer mass ratios used for the composite, the relative efficiencies improved compared to the M3EH-PPV single layered devices. The optimum relative efficiency was obtained for a nanotube mass ratio of 1.2 %. As regards the use of MWNT in polymer solar cells, we measured the photovoltaic response of cells using the PmPV+MWNT composite and a thin MEH-PPV buffer layer in a sandwich structure with ITO as the anode and Al as the cathode. Moreover, an ITO / M3EH-PPV+MWNT / I^{3-}/I^{-} / Pt photoelectrochemical cell was prepared and characterised. The presence of MWNT widened the optical active layer and increased the power efficiency by an order of magnitude compared to a cell without MWNT, while increased short-circuit density in polytertiophene based photoelectrochemical cells with MWNT was observed. We concluded that the carbon nanotubes allowed electrons to be transferred and efficiently transported, via their continuous conductive network, to the collecting electrode





Lasers have become common in daily life and are even being incorporated into the playthings. Protection from lasers is therefore not only a scientific subject but also a potential social issue, which motivates much interest in research on optical limiting materials. An ideal optical limiter should strongly attenuate intense and potentially dangerous laser beams, while exhibiting high transmittance for low intensity ambient light. The CNTs have been found to show outstanding nonlinear optical (NLO) extinction to high intense laser beam, which could serve as an optical limiting material for laser protection application. We have also investigated the NLO properties of single-walled carbon nanotubes (SWNTs), aiming to the development of industrially applicable CNT-based nonlinear photonic devices, especially, optical limiters. As opposed to the reverse saturable absorption (RSA) materials, e.g., phthalocyanines, porphyrins, and $C_{60.}$ CNTs have broad band optical limiting effect, resulting from the thermally-induced nonlinear scattering, covering from the visible to the near infrared. In an effort to realize the applicable CNT-based optical limiters, we start to investigate the potential effect factors to the optical limiting performance of pure CNTs. The optimization of CNT materials for optical limiting is carried out through suppressing the negative effects. Each material possesses not only advanced properties but also some intrinsic defects, which could not cover all requirements of optical limiting applications. Further improvement of optical limiting ability can be done by introducing the other functional components to combine with CNTs. The reverse saturable absorbers have a quick response time in the picosecond regime characteristic of electronic interactions, while carbon nanotubes associate with scattering generally respond at best in the nanosecond regime. The complementary temporal and spatial NLO characteristics of nonlinear absorber compounds and carbon nanotubes motivate the development of nonlinear absorber-carbon nanotube hybrids by covalent or noncovalent combination. Furthermore, the thin film structures are very suitable for the integrated photonic devices. The study of NLO properties of CNT-based composites in solid thin films is an important stage for the development of industrially applicable photonic devices.



Nonlinear extinction coefficients (a), optical limiting effects (b), and scattered intensities (c) of SWNT dispersions in NMP, DMF, and DMA, respectively.

Nanotubes Based Polymer Optoelectronics

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Carbon nanotubes (CNTs) exhibit strong saturable absorption, i.e. they become transparent under sufficiently intense light. This has great potential for applications in photonics. By tuning the nanotube diameter it is easy to tune the saturable absorption in a broad optical range of interest for telecommunications, medicine and military applications. CNTs also have sub-picosecond relaxation times and are thus ideal for ultrafast photonics. The performance of CNTs based saturable absorbers strongly depends on the CNTs concentration, size of CNT bundles, and transparency of the matrix where CNTs are dispersed. CNT saturable absorbers can be produced by cheap wet chemistry and can be easily integrated into polymer photonic systems. The performance of CNTs based saturable absorbers strongly depends on concentration, the size of CNT bundles, and transparency of the matrix.

Here, we review the fabrication and characterization of saturable absorber based on CNT - polymer optical composites [1,2,3]. We use strong ultrasonication to obtain CNT solutions. Such solutions with different nanotube bundle sizes are then studied by photoluminescence excitation spectroscopy [4]. We find that exciton energy transfer between semiconducting CNTs is an efficient carrier relaxation channel in the bundles [4]. This fingerprints and quantifies the presence of small bundles and allows us to optimise the solutions used for composites preparation. The saturable absorption properties of such composites are studied with a femtosecond laser. We demonstrate picosecond pulse generation in a nanotube mode-locked waveguide laser [5], as well as 600 fs generation in an erbium doped fiber laser [1]. We also report a novel SWNT- polycarbonate polymer composite, with an absorption maximum at 1550 nm and a bandwidth of about 300 nm [6]. The composite shows strong saturable absorption with saturation intensity of 7 MW/cm^2. We also demonstrate the first SWNT-mode-locked widely tunable fibre ring laser [7]. This is achieved through the control of amplification at the specific transitions of the Er^{3+} gain medium by placing a band-pass filter in a laser cavity [7]. Besides the wide tuning range, this laser also features a high optical signal-to-noise ratio and an excellent jitter performance.

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DESIGN AND PROPERTIES of CARBON NANOTUBE-BASED ULTRAFAST BEAM MODULATORS FOR MID-INFRARED LASERS

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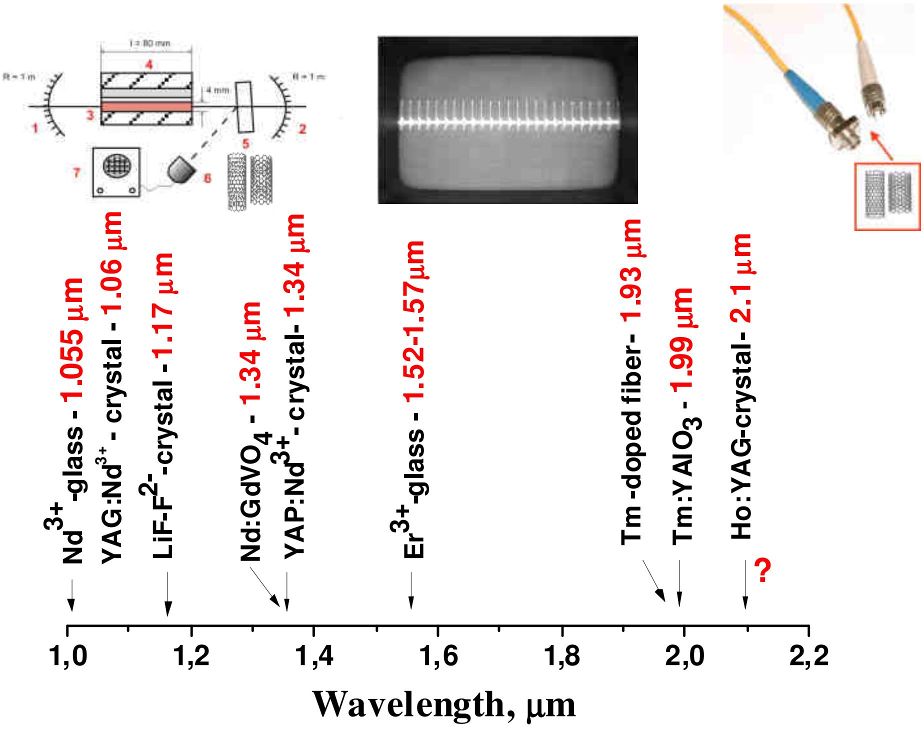
A high optical non-linearity and ultrafast relaxation times of single-wall carbon nanotubes (SWNTs) and different media incorporating them, have allowed to create a new family of non-linear optical elements – saturable absorbers for different solid state lasers (including the fiber ones) [1-6]. One of the key advantages of nanotubes is their ability to work in a wide spectral range. Up to now SWNTs synthesized by different techniques (arc discharge, laser ablation, CVD from methane or ethanol, HiPCO- high pressure CO decomposition, etc.) covered the range from 1 to 2 µm (*see Figure*). Recently developed CVD technique of SWNT synthesis on ferrocene in CO gas provides an extension of the absorption range up to 2.7 mkm [4]. This should allow involving into consideration a few lasers with the working wavelengths longer than 2 µm (for instance, Ho:YAG laser-2.1 µm).

In this paper the fundamental and practical aspects of SWNT-based optical elements will be discussed. A special attention will be paid to our achievements in development of the formation techniques of such elements, in the adjustment of their spectral range to the working wavelength of the fixed lasers, in the ways of the output laser pulse shortening and in the laser damage threshold increasing.

The work was supported by RFBR and RAS projects.



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STRUCTURED POLYMER/NANOCARBONS COMPOSITE MATERIALS FOR PHOTONICS

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The discovery of a very efficient photoinduced electron transfer from conjugated polymer (CP) to [60]fullerene opened up new aspects with potential applications of nanocarbons in fotonics, non-linear optics, optoelectronics and organic photovoltaics (PV). The core of PV devices is the interpenetrating biscontinuous donor/acceptor molecular network, where CP acting as a donor (D) and nanocarbon materials (NCM) acting as an electron acceptor (A). An anisotropic property of the CP/NCM blend film is extremely important for increasing the power conversion efficiency PVs [1].

A series of NCM has been synthesized: C_{60}; asahomo[60]fullerenes and (4-6) poly(amino)[60]fullerenes; [60]fullerene dimmers; single-walled carbon nanotubes. The structure of the NCM was studied by cyclic voltammetry, ^{13}C NMR-, UV-VIS-NIR-, FTIR-, Raman spectroscopy [2-4]. Photoluminescence experiments, current-voltage measurements were performed on sandwich type cells based on CP [MEH-PPV, P3HT] and CP/NCM blend films to investigate the charge transfer process. Preliminary results indicate that NCM under investigations have a great potential for use as electron acceptors in polymeric solar cells. Series of microscopy methods TEM and AFM (tapping mode) has been used to investigate CP/NCM blend film microstructure. The morphologies of NCM under investigation and C_{60} species in MEH-PPV matrix are sufficiently different. Thus, we seen that asahomo[60]fullerene derivative formed linear extended structures (rod-like formations - thickness is approximately 100 nm and length of several micrometers), as well as C_{60} formed a ball-shaped aggregates with dimensions around 10 nm. Microstructure – properties correlation of the CP/NCM blend film were discussed. Also, we discuss the way of increasing anisotropic properties of the polymeric matrix by means of design of NCM and D-A self-organization towards the desired nanomorphology of the composite film.

The work was supported by Program for fundamental studies of Presidium of the Russian Academy of Sciences “Fundamental Problems of Physics and Chemistry of Nanometric-Scale Systems and Materials”.

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ULTRAFAST LIGHT-INDUCED CHANGE OF ABSORBANCE IN POLYMER FILMS WITH EMBEDDED CARBON NANOTUBES

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Last years, nano-carbon composites have attracted an attention due to their unique mechanical and electronic properties. One trend is focused on fabrication of light-weight ultra-strong materials, another one is concentrated on designing of highly flexible transparent conductors and semiconductors for organic electronics. Recently a strong optical non-linearity has been revealed in nano-carbons [1]. This is very promising for their application as ultra-fast light modulators in solid-state lasers (in bulk and fiber schemes) [2,3]. Here we report time-resolved femtosecond measurements of an anomalous light-induced change of absorbance of organic film with embedded carbon nanotubes.

Single-wall carbon nanotubes (SWNTs) synthesized by a high-pressure CO decomposition method (HiPCO) and arc-discharge process (arc) were homogeneously distributed in a polymer cellulose film [4] with concentration of 0.01% (wt). The film thickness was 5 μm. The presence of well-defined narrow bands in the transmission spectrum of the film (see Fig. 1) indicates that SWNTs are well separated from each other in the polymer matrix.

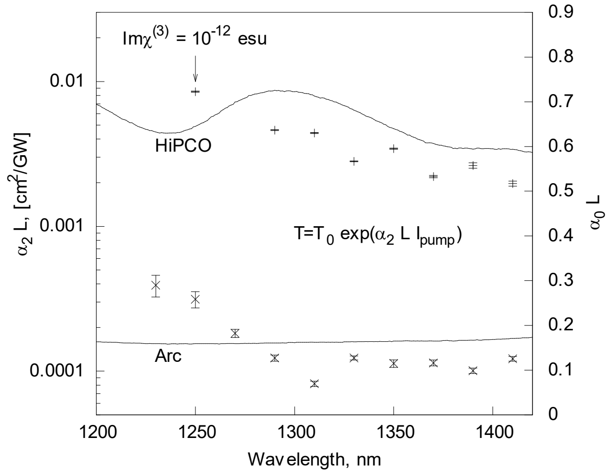

Fig 1: Wavelength dependence of the linear *(solid line)* and nonlinear *(points)* absorption for the arc and HiPCO nano-tube films.

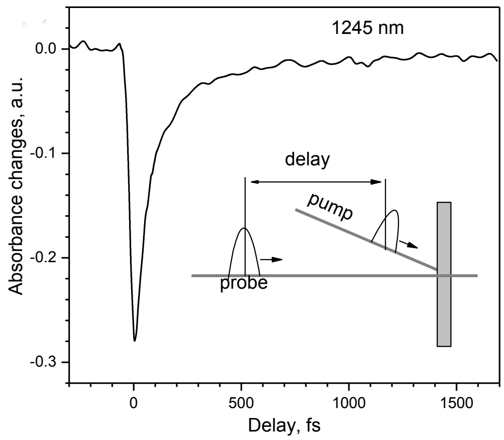

Fig 2: Absorbance changes in nano-carbon film as a function of delay between pump and probe pulses.

We investigated the absorbance changes of the film under irradiation by femtosecond laser pulses at wavelengths of 1200-1400 nm (see Fig. 1). A temporal evolution of the induced absorption change is shown on *Fig. 2*. The observed maximum of the light-induced absorbance change for HiPCO film corresponds to the nonlinear optical susceptibility of SWNT film of $\mathrm{Im}\chi^{(3)} \approx 10^{-12}$ esu. The characteristic times of the fast and slow components of the nonlinear response were about 200 fs and 5 ps, respectively.

The observed anomalous light-induced absorbance change makes SWNT-based composites a promising material for the passive mode-locking in femtosecond solid-state and fiber lasers.

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OPTICAL NONLINEARITY IN THIN FILMS AND SOLUTIONS OF C_{60}-ZN(II) TETRAPHENYLPORPHYRIN COMPLEXES

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We have studied nonlinear optical properties and photoluminescence kinetics in solutions and thin films of Zn(II) tetraphenylporphyrin and C_{60}-Zn(II) tetraphenylporphyrin complexes. Among the fullerene-containing dyads, the ones with porphyrin display improved nonlinear responses. We have developed the vacuum deposition technique for producing thin films of these compounds and shown that the enhancement of optical nonlinearity is not necessarily connected with the formation of covalent bonds between the components.

Ab initio quantum chemical calculations have shown that due to the acceptor properties of C_{60} molecule, the pair C_{60} - ZnTPP forms a stable charge transfer complex with a binding energy of 0.6 эВ, distance between the molecular components of 0.25 nm and the amount of transferred charge of 0.4 ē. The central zinc atom has the charge of +0,383 ē and is shifted by 0.065 nm from the plane of the porphyrin ring towards the C_{60} cage. The formation of complexes is predicted to enhance the nonlinear response due to the shift of the π–electron density and increased polarity both for porphyrin and fullerene molecules. We have measured the absorption profile in the range $2\cdot10^{-5}$ - 1 J/cm^2 at the wavelength of 560 nm, which corresponds to the maximum of the Q-band absorption of porphyrin. A comparative study is made for toluene solutions of: (i) C_{60} with $2\cdot10^{-4}$ mol/l concentration; (ii) ZnTPP with $5\cdot10^{-5}$ mol/l concentration and (iii) a joint solution C_{60}-ZnTPP with the molar ratio 4:1. Similar study has been performed for the thin films of pristine components and the mentioned complex, which were grown by in the quasiequilibrium conditions on the CaF_2 substrates. A large increase of the absorption intensity (darkening) is found on the formation of the charge transfer complex.

The photoluminescence kinetics for the toluene solutions and thin films has been explored both on the wavelength of 560 nm corresponding to the absorbance maximum for free ZnTPP molecule and 343 nm where the C_{60} molecule has the maximum. We have found that the photoluminescence time decay is an order of magnitude lower for the ZnTPP thin solid films than that for the ZnTPP toluene solutions. The time decay constant is found to be 300 ps, which is typical for the π*-π transitions. We have found a phenomenon of luminescence condensation in the pumping field with the increase of pumping energy. This phenomenon reveals itself in the effect that on exposing the medium with the light pulses having the duration close to or less than the spontaneous luminescence time, the response duration decreases with the increase of the stimulating emission power density.

CONFINEMENT OF OPTICAL LIMITING OF ONION-LIKE CARBON BY LASER INDUCED OPTICAL BLEACHING IN N,N-DIMETHYLFORMAMIDE.

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Onion-like carbon (OLC) produced via annealing of explosive nanodiamond (ND) are perspective for the development of optical limiting materials [1]. Here we have studied the interaction of laser irradiation (λ=1064 nm) with OLC suspension in *N*,*N*-dimethylformamide. The suspensions of OLC sample were previously characterized by PCS to estimate size of aggregates, TEM and UV-Vis spectroscopy. It has been found that the OLC structures exhibit strong optical limiting action if one use defocused laser irradiation while usage of focused laser radiation results in the optical bleaching of OLC suspension. Thus at high power laser irradiation the effect of bleaching overcomes the optical limiting of OLC. The results are discussed in terms of photoinduced electron transfer reaction of curved OLC shells with H-donor DMF molecules. This reaction can be used for surface functionalization of OLC.

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PHOTO-INDUCED ABSORPTION ON CARBON NANOTUBES

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We studied the photo-induced transmission change (ΔT/T) upon quasi-continuum laser excitation in films of (6,5) enriched Comocat single wall nanotubes (SWNTs) embedded in a polymeric matrix. This technique probes long-lived excited species, with lifetime in the 1-100 ms time domain.

We observe a complex line-shape in ΔT/T spectra, that can be assigned to a superposition of bleaching and absorption modulation. We speculate photoexcitation creates long living charged states, trapped at the tube surface. We assume holes, resulting from excitons dissociation, tend to move to the polymeric matrix leaving a total negative charge on tube. Their effect could be a diameter expansion of the SWNTs [1] with a consequence blue shift of the first optical transition [2], as observed in our spectra.

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LINEAR AND NONLINEAR OPTICAL PROPERTIES OF PHTHALOCYANINE-CARBON NANOTUBE BLENDS

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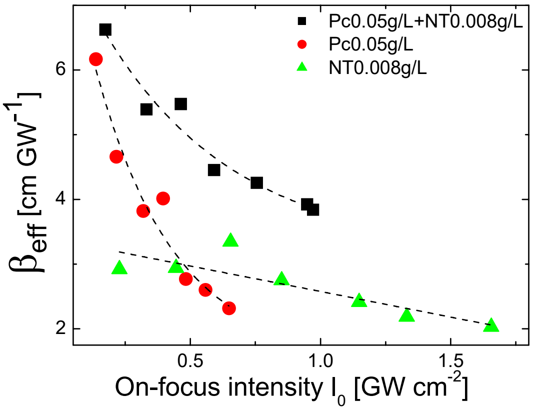
Carbon nanotubes (CNTs) have been extensively studied as viable optical limiting (OL) materials [1-3]. The OL effect in CNTs results from thermally-induced nonlinear scattering, covering a broad wavelength range from the visible to the near infrared. Reverse saturable absorber phthalocyanines (Pcs) have a quick response time in the picosecond regime, while CNTs associate with scattering generally respond at best in the nanosecond regime. Merging the complementary temporal and spatial nonlinear optical (NLO) characteristics of Pcs and CNTs has resulted in the development of nonlinear absorber-CNT hybrids by covalent or noncovalent combination.

Stable zinc Pc-CNT composites were prepared by blending ZnPc solutions and CNT dispersions. The addition of CNTs does not affect the linear absorption bands, but results in a significant fluorescence quenching of Pc molecules. The NLO properties of these nanocomposite systems were characterized using the open aperture *Z*-scan technique with nanosecond pulses at 532 nm. The ZnPc-CNT composites exhibited unique NLO properties when compared with separate Pc solutions and CNT dispersions. The CNT dispersions in DMF can improve the nonlinear extinction (NLE) of the whole system more effectively than the NMP dispersions. Most noticeably ZnPc-CNT composites enhanced the effective NLE coefficients, β_{eff}, in the higher energy density region when compared to the Pc solutions, as shown in the figure. Therefore the low and high energy density NLE repsonse could be attributed as such: Pcs influenced the OL effect in lower energy density region, while the CNTs played a more critical role in the attenuation of incident laser light in higher energy density region. Part of results was submitted to *Optics Express* [4].



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Friday, August 8

Thermionic and field emission from nanostructured diamond and carbon films

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Nanocrystalline diamond and carbon nanostructures can be prepared which exhibit strong field enhancement and field emission. Moreover, nanocrystalline diamond surfaces can achieve a negative electron affinity and thermionic emission has been detected at temperatures less than 500C. In this presentation, the relation of the nano-scale structure to the work function, the Fermi level, and the field penetration effects are considered to describe the thermionic and field emission from these carbon materials. A combination of advanced surface microscopy and electron spectroscopy measurements are described to characterize the electron emission. Results establish that N-doped, hydrogen terminated diamond films can exhibit a work function of less than 1.4 eV and show uniform thermionic emission properties. It is shown that the nanostructure properties of the film significantly affects the emission properties. For S-doped nanocrystalline diamond, intense emission sites are observed which exhibit temperature dependent properties. Nanostructured carbon films exhibit similar properties. The field emission and thermionic emission are analyzed to establish the work function of the two processes. The results indicate that carbon materials could be employed in a range of electronic and optoelectronic devices and also for direct conversion of heat into electrical energy.

Cold and laser stimulated electron emission from nanocarbons

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Various types of electron emission from condensed matters are used for creation of electron beam sources in vacuum electronic devices such as X-ray, and cathode-ray tubes, microwave devices etc. Study of the electron emission phenomena is an important tool for evaluation of fundamental properties and peculiarities of the materials. Carbon based materials have been the focus of many studies of their electron emission properties. This is particularly because of strong atomic bonding in graphite and diamond which provides chemical inertness and sustainability of carbon cathodes under action of residual gas ion bombardment. Besides different carbons great attention has been attracted last time to its nanostructured forms. Carbon nanotubes exhibit field (or cold) emission characteristics which are typically attributed to the geometric effects, and other more complex effects associated with field penetration, electronic structure and stationary states. Nanocrystalline diamond films have displayed similar field emission characteristics at relatively low applied fields, and this effect has been related to the amount of graphitic carbon inclusions. The field enhancement from these nanodiamond films has been attributed to both morphological effects and grain boundary conduction. In this lecture we will review basic theoretical approaches, computer simulations and experimental studies of the electron emission from nanocarbon materials.

The electron emission thresholds and currents were calculated for different shapes of nanosized emitters to evaluate their dependencies on density of emission sites. It is shown that plate-like nanographite emitters may provide higher stability of current with thresholds comparable to that for cylindrical carbon nanotubes. The computer simulations reveal dependence of current-vs-voltage characteristics of nanocarbon cathodes on statistical distribution of geometrical characteristics of the emission sites.

The experimental comparative studies of field emission from carbon nanotubes and nanographite films have exhibited general and specific properties of these nanocarbon emitters. In particularly, mechanical flexibility of the nanotubes is responsible for excitation of self oscillations. The mechanical oscillation of carbon nanotubes leads to emission current instabilities depending on geometrical parameters of the emitters.

The effect of laser radiation on the electron emission from the nanographite cathodes has been studied. Under irradiation of the cathodes by nanosecond laser pulses the emission current density is increased up to 10 A/cm^2. In the femtosecond regime, the laser excitation creates in the nanographite cathode hot electrons. There are not enough time for the femtosecond pulses to transfer energy from electrons to the lattice before escaping into vacuum. Such a hot electron emission from cold cathode provides extremely dense femtosecond electron bunches with current densities up to 10^3 A/cm^2.

The device applicability of the nanocarbon cathodes is demonstrated for vacuum fluorescent lamps, flat panel prototypes and X-ray tubes.

Graphite intercalation compound KC_8 revisited: a key to graphene

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Electrons in individual graphene layers are a prototype of a two-dimensional gas of massless Dirac Fermions [1]. In realistic devices, however, the electronic properties are modified by elastic deformations, interlayer coupling, substrate interaction [2] or correlation effects [3]. Here we unravel the electronic structure of doped graphene by revisiting the stage one graphite intercalation compound KC_8 using a combined angle–resolved photoemission spectroscopy and ab–initio study. We prove an almost complete charge transfer to the graphene layers yielding a Fermi level shift of the Dirac point by 1.35 eV. The full experimental dispersion is in excellent agreement to GW calculations of doped graphene. This highlights that AA stacked graphene sheets in KC_8 have negligible interlayer coupling. Thus Dirac Fermion behaviour is preserved and for the first time we directly determine the full experimental Dirac cone of graphene. In addition we prove that superconductivity in KC_8 is mediated by electron–phonon coupling to a TO phonon, yielding a strongly renormalized quasiparticle dispersion close to the Fermi level. Thus we provide crucial input for understanding both the unique properties of graphene and superconductivity in KC_8.

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NANO-CARBON CVD FILMS: OPTICAL CHARACTERIZATION OF DEPOSITION PROCESS AND MATERIAL PROPERTIES

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The remarkable flexibility of the chemical vapor deposition (CVD) process allows one to create materials with dramatically different properties by changing the geometry of reaction chamber and discharge type. Moreover, in our previous works we shown that a controllable growth of various thin film carbon materials, including diamond, graphite, and nanotubes can be achieved in the same direct current (DC) discharge CVD system by changing pressure and composition of hydrogen-methane mixture along with substrate temperature, discharge current and voltage [1, 2].

In this work correlation of CVD process parameters with structure and composition of deposited carbon films via using various experimental techniques (Optical Emission Spectroscopy, Raman Spectroscopy and SEM) was investigated.

Optical emission spectra (OES) from CH_4/H_2 DC discharge glow plasmas, which are used for the deposition of carbon thin films, have been characterized. Identified species include CH, H, H_2, C_2 and CN (Fig.1 and Fig.2). Variation between spectra from H_2/CH_4 and $H_2/CH_4/N_2$ plasmas are discussed. The observed OES variation of the $CH_4/H_2/N_2$ plasma with CH_4/H_2 and N_2/H_2 ratio correlated with films characteristics and morphology.

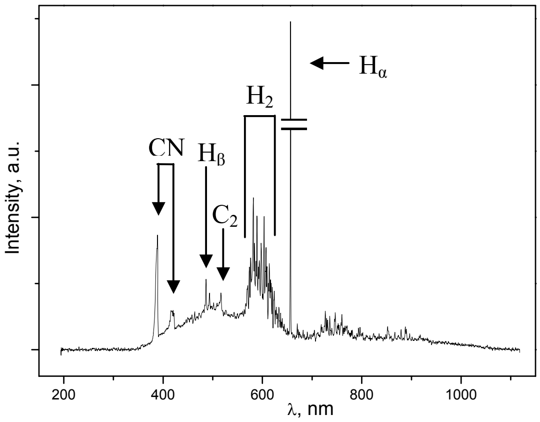

Fig.1. Typical OES for CH_4/H_2 mixture plasma with 10% methane. The total gas pressure is 90 torr, applied voltage is 700 V and dicharge current is 7A. Spectra taken 1 mm above the substrate surface.

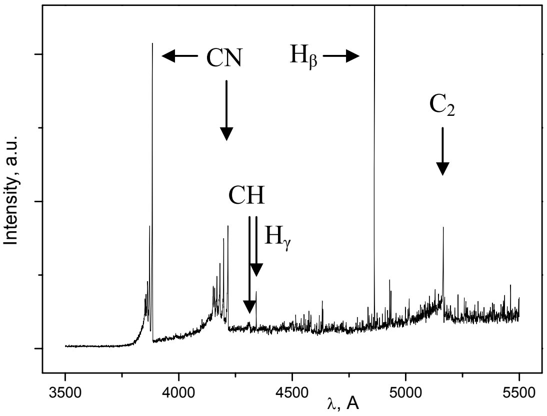

Fig.2. High-resolution OES in range 3500-5500 Å for CH_4/H_2 mixture plasma with 10% methane. The total gas pressure is 90 torr, applied voltage is 700 V and dicharge current is 7A. Spectra taken 1 mm above the substrate surface.

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INTERACTION OF CARBON LINEAR CHAINS WITH SILVER ISLAND FILM STUDIED BY SURFACE-ENHANCED RAMAN SCATTERING

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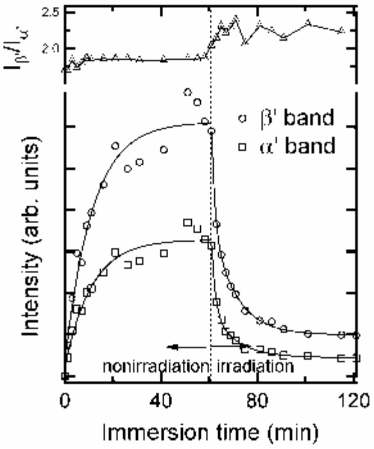
Carbon linear chains (polyynes) which consist of sp hybridized carbon atoms and hydrogen termination represent the system with unique physical and chemical properties. Much attention has been paid to their optical properties such as ultraviolet absorption, Raman scattering, and photoluminescence [1,2].

Recently, we investigated a series of size-separated polyynes solution by using normal Raman (NR) and surface-enhanced Raman scattering (SERS) spectroscopy [1], and revealed that spectral features in SERS spectra are much different from those in NR spectra. In the SERS spectra, besides a prominent band (α' band) located at around 2000 cm^{-1} region, which is characteristic of stretching modes of carbon chain and also seen in NR spectra, another strong band (β' band) appears near the α' band. It is probably due to the interaction between polyyne and silver island film used as a SERS enhancer. However, the origin of the β' band is not yet clear.

In the present work, we investigate the time evolution of polyyne $C_{14}H_2$ SERS spectrum after immersing silver island film into polyyne n-hexane solution. Figure shows the plots of the integrated intensities of the α' and β' bands in the SERS spectra as a function of the immersion time. Relative intensities of the α' band to the β' band are also plotted. For the first 61 min, a laser beam did not irradiate on the silver island film except for the accumulation time (10 sec.) of the SERS measurement. After then, the sample was irradiated continuously. The intensities of the α' and β' bands increased and then saturated with increasing the immersion time in the first period and dramatically decreased in the second period. These behaviours indicate adhesion and degradation of polyynes on the silver island film, respectively. The relative intensities of the α' band to the β' band were constant during the first period. This result strongly suggests that the β' band has the common origin with the α' band.



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OPTICAL DIAGNOSTICS of TEXTILE FIBERS CONTAINING SINGLE-WALL CARBON NANOTUBES

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Single-wall carbon nanotubes (SWNTs) represent a new nanoscale material possessing unique physical and chemical properties. Already today the nanotubes are widely used in nanoelectronics, nonlinear optics, vacuum electronics (as cathodes for displays), biomedicine.

Unique mechanical characteristics of SWNTs (a high strength and elasticity, a feather-like weight) and a high capacity for energy absorption already have been used for manufacturing of high-strength composite materials in air- and mechanical engineering. In this work we tried to introduce SWNTs into the modern polymeric materials used for creation of antiballistic fabrics.

As a starting point we used the technique developed earlier for preparation the aqueous suspensions of individual SWNTs. The nanotubes for our experiments have been synthesized by arc discharge technique [1]. The suspensions contained the raw SWNTs, have been treated by ultrasonic together with surfactants (for instance, SDBS-sodium dodecyl benzene sulfonate). This process has been followed by ultracentrifuging (with acceleration of 130000 g). A top light fraction containing single nanotubes or small (2-3 SWNTs) has been separated [2,3]. The separated suspension was introduced into aramid fibers either during polymerization, or after, during processing a polymeric fiber. A complex optical diagnostics (combined Raman spectroscopy and UV-VIS-NIR optical absorption) was used at each step of the fiber formation. Thin films have been formed on the base of composites obtained. Their strength has been measured by standart methods. The correlations between the strength and the nanotube content have been revealed.

The work was supported by RFBR and RAS Programs.

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DECAYTIMES OF FREE EXCITONS IN SYNTHESIZED HIGH-QUALITY DIAMOND CRYSTALS

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Diamond is a wide-gap semiconductor having an energy gap of 5.49 eV in the deep ultraviolet region. In high-quality single crystals of diamond, the edge emission is dominated by phonon-assisted recombination of free excitons [1]. Temperature dependence of the decaytimes of the free excitons in a low-density regime has been discussed in Ref. [2]. We have investigated the decay kinetics of free excitons at high-density such that an electron-hole droplet phase appears [3], by following the transients of the edge emission under band-to-band excitation using femotosecond laser pulses.

The samples were synthesized by a high-temperature high-pressure method. Figure 1 shows a representative spectrum of the edge emission under photo-excitation at 214 nm of a high-purity diamond crystal with boron and nitrogen concentrations less than 0.1 ppm. Shown in the inset are transients of the TO phonon assisted recombination of free excitons at different excitation power densities. We found that the free excitons decay faster with a decreasing density. On the other hand in crystals containing 0.1-0.9 ppm boron or nitrogen, the excitons decay even faster, i.e., within 10 nanoseconds. In order to understand the physical origin for the density dependence and the effect of doping, we model the transients using a coupled rate equations. It is found that the capture of free excitons to bound states due to impurities or to electron hole droplets play an important role in determining the kinetics of free excitons.

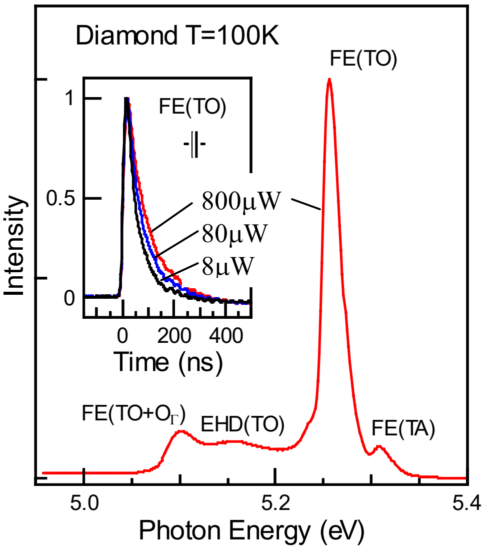

Fig. 1 Luminescence spectrum of high-purity diamond at 100 K. Inset: transients of the FE(TO) line with different excitation densities.

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ELECTROCHEMICALLY TUNED PROPERTIES OF ELECTROLYTE-FREE CARBON NANOTUBE MATERIALS

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Injecting high electronic charge densities can profoundly change optical, electrical, and magnetic properties of the material. Such charge injection in bulk materials has traditionally involved either dopant intercalation or the maintained use of a contacting electrolyte. We demonstrate tunable electrochemical charge injection and charge retention in the absence of applied field for bulk carbon nanotube materials without the needed for either volumetric intercalation of ions or electrolyte contact. Application is demonstrated for tuning the electrical conductivity and electron field emission of carbon nanotubes, as well as for supercapacitors that store charge without the presence of electrolyte.

INTERACTIONS OF ULTRASOFT X-RAYS WITH CARBON NANOTUBES

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Carbon nanotubes (CNTs) are among the most promising elements of future nanotechnologies. A vast amount of information on the structure and properties of CNTs obtained in the past 15 years point to considerable potential for application of these unique structures in nanoelectronics, energetics, medicine, and other high-technology industries. One of the most important problems is to produce ordered CNT arrays with desired texture and properties. Arrays of CNTs aligned perpendicular to the substrate surface have strong anisotropy of mechanical and electrical properties and are used for fabricating planar field emitters, electrochemical electrodes, sensors, etc. Several methods are available for characterizing the texture of aligned CNT arrays. Information on the distribution of nanotube directions in an array can be obtained from Fourier transformation of the lateral cleavage image. Anisotropy of the optical response of fundamental vibrational modes was observed in the Raman spectra of CNT arrays and in the optical absorption and fluorescence spectra of aligned CNTs. Unfortunately, because of a large optical wavelength, these methods are insensitive to ordering in domains smaller that 100 nm. Orientation of graphite layers in multi-walled CNTs can be determined by X-ray diffraction. However, this method is applicable only for well-graphitized nanotubes. Angle-resolved X-ray spectroscopy is free of most of the above limitations. Measuring the angular dependences of X-ray emission and absorption spectra of graphite allows the determination of its texture. Similar to graphite, CNTs are also characterized by chemical bond anisotropy; however, the angular dependence of the spectra of aligned CNTs is less pronounced than for graphite because of high structural disorder in CNT samples. Carbon K-edge X-ray absorption spectra of the aligned MWNT films were measured. The angular dependent changes observed for the spectral profiles were interpreted in terms of variation of π- and σ-contributions depending on the take-off or incidence angle of X-ray radiation. Measurements of angle dependence of X-ray fluorescent and X-ray absorption spectra from a film of aligned single wall carbon nanotubes allowed estimation of their ordering in the arrays. The theoretical model considering the deflection of orientation of cylindrical tubes from the normal to the substrate have been developed and used for calculation of theoretical angular dependences. The $\pi*/\sigma*$ intensity ratio was used for determination of the SWNT film texture from the comparison between the calculated and experimental data.

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