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# Proceedings

UNIVERSITY OF
EASTERN FINLAND

Third International Workshop

## Nanocarbon Photonics and Optoelectronics

29 July - 4 August 2012, Holiday Centre ”Huhmari”
Polvijärvi, Finland

Joensuu, 2012

University of Eastern Finland
Department of Physics and Mathematics

# Proceedings

# Third International Workshop
# Nanocarbon Photonics and Optoelectronics

Holiday Centre ”Huhmari“, Polvijärvi, Finland

Editors:
Yury Svirko
Dmitry Lyashenko

Finland

29 July-4 August 2012

# NPO2012 Schedule-at-a-Glance

| | **Sunday July 29** | **Monday July 30** | **Tuesday July 31** | **Wednesday August 1** | **Thursday August 2** | **Friday August 3** | **Saturday August 4** |
|---|---|---|---|---|---|---|---|
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| *9:45-10:30* | | Oral presentations | Oral presentations | V. Klimov | Oral presentations | Oral presentation | |
| *10:30-10:45* | | Coffee Break | Coffee Break | Coffee Break | Coffee Break | Coffee Break | |
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# Welcome

The ever growing interest of the photonics community to nanocarbon materials is major driving force of the series of International Workshops on Nanocarbon Photonics and Optoelectronics established in 2008. The NPO Workshops aim at an intensive and informal ideas exchange between senior scientists, young researchers and students. The Workshops provide an opportunity for students and post-doctoral researchers to learn more about both fundamentals of nanocarbon materials and the latest achievements in this rapidly developing field.

NPO2008 and NPO2010, which were held in the in Eastern Finland in August 2008 and 2010, respectively, had attracted about 100 researchers and students from around the globe. The proceedings of the Workshops have been published in the special issues of Journal of Nanoelectronics and Optoelectronics and are available for free downloading.

We are pleased to welcome you to the Third Workshop “Nanocarbon Photonics and Optoelectronics”, which will be held at holiday centre “Huhmari”, Polvijärvi, Finland. The NPO2012 venue is situated on the shores of the lake Höytiäinen, which broad waters and numerous islands provide you with magnificent scenery.

We are grateful to our sponsors for their financial support, which has enabled us to reduce participation costs for all attendees and to provide travel grants to our lecturers. We hope that the NPO2012 will continue and extend success of two previous Workshops and will allow all participants to enjoy the beauty of Scandinavian summer.

NPO2012 Co-Chairs
Yuri P. Svirko,
Department of Physics and Mathematics,
University of Eastern Finland

Alexander N. Obraztsov,
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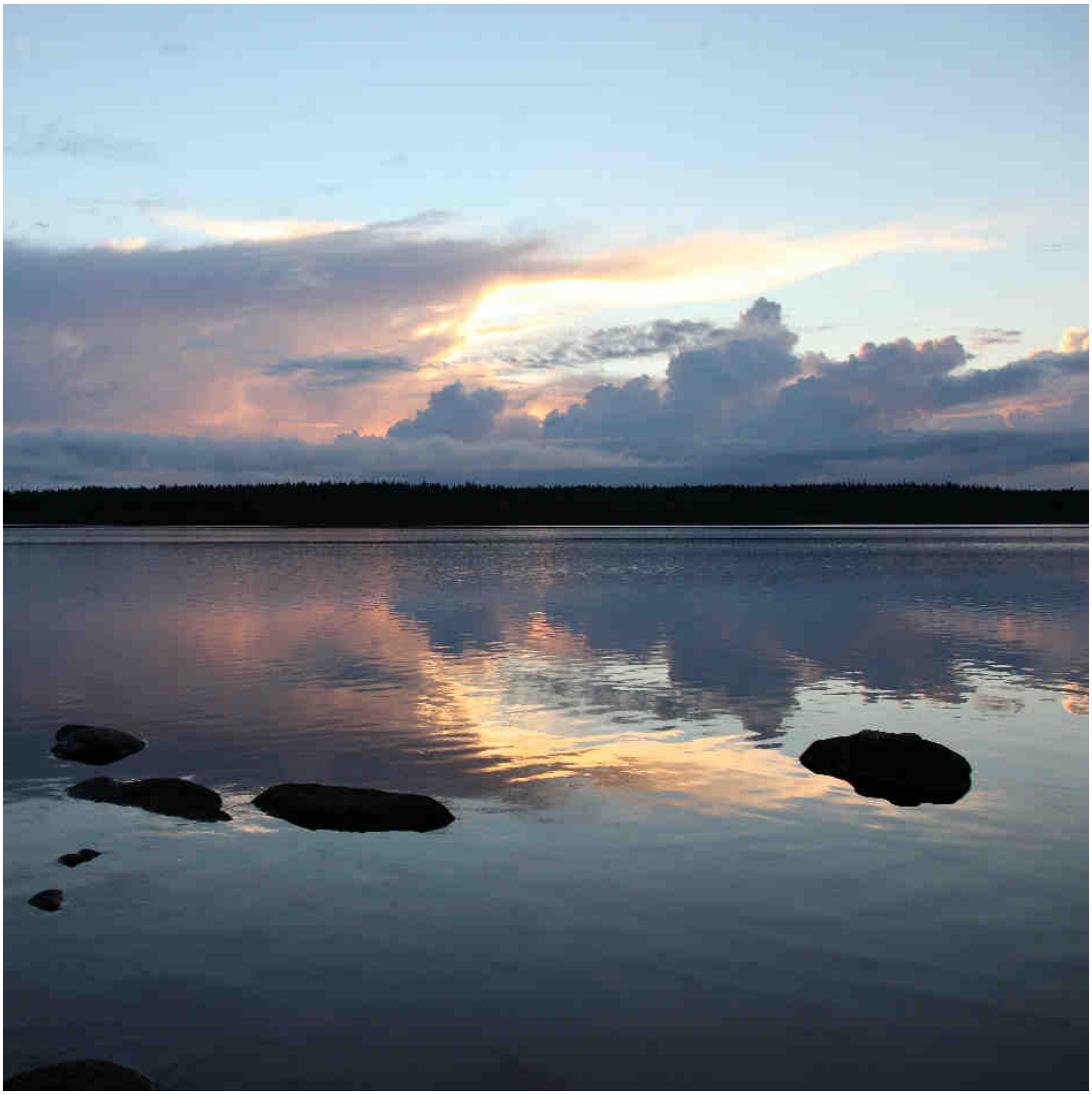
M.V. Lomonosov Moscow State University

# Contents

# Monday, July 30



# Seeing electrons in two dimensions: Optical spectroscopy of graphene

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Optical spectroscopy provides an excellent complement to transport measurements as a means of understanding the distinctive properties of electrons graphene. Within the simplest description, one has for the graphene monolayer a zero-gap semiconductor with direct transitions between the conical bands. This gives rise to a predicted absorption that is frequency independent and has a strength of $\pi\alpha = 2.3\%$, where $\alpha$ is the fine-structure constant. This prediction is indeed satisfied in an appropriate spectral range in the near infrared [1], but that at higher photon energies band-structure and electron-hole interactions significantly modify this result, leading to the formation of a saddle-point exciton [2].

Optical absorption spectroscopy also permits a detailed analysis of how the linear bands of graphene are modified through interlayer interactions. In particular, graphene bilayers, with their lowered symmetry support a band gap under the application a strong perpendicular electric field. Such a tunable band gap, with a magnitude up to 200 meV, has been observed by infrared measurements [3]. For the case of few-layer graphene samples, more complex 2D band structure develops, as can be traced through the optical absorption spectra and their critical points [4,5,6].

Another important aspect of laser spectroscopy is the ability to examine the dynamics of fundamental excitation in graphene by time-resolved techniques. We describe measurements on femtosecond electron dynamics based on measurement of the light emission from graphene induced by femtosecond laser pulses [7]. The studies reveal very rapid electron thermalization, as well as equilibration with strongly coupled optical phonons. This stage is followed, on the picosecond time scale, by cooling through anharmonic phonon decay [8].

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# RAMAN SPECTROSCOPY OF INDIVIDUAL DOUBLE-WALLED CARBON NANOTUBES

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The combination of transmission electron microscopy, electron diffraction and resonant Raman spectroscopy on individual suspended nanostructures is the ultimate method to relate unambiguously theirs structural parameters [1], optical transitions [2, 3], and Raman-active phonons [1, 3, 4].

This approach has been successfully used to study the main Raman-active modes of individual double-walled carbon nanotubes [5] (DWCNT). In this contribution, we will show, in particular, that low-frequency features in the Raman spectra cannot be connected to the layer diameters d by means of the 1/d power law, widely used for the diameter dependence of the radial-breathing mode of single-walled nanotubes. We discuss this disagreement in terms of mechanical coupling between the layers of the DWCNT, which results in collective vibrational modes. The mechanical coupling qualitatively explains the observation of Raman lines of breathing-like modes, whenever only one of the layers is in resonance with the laser energy.

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# OPTICAL AND MAGNETIC PROPERTIES OF ENCAPSULATED SINGLE-WALLED CARBON NANOTUBES

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One-dimensional forms of nano-carbon attract a great interest last years. Single-walled carbon nanotubes (SWCNTs) possess unique electrical and photonic properties. All of these properties depend on the geometries of certain nanotubes. Significant progress in applications of carbon nanotubes has been achieved after the appearing of the possibility to separate carbon nanotubes in large scale by diameter and electronic structure, in particular, by conductivity type [1]. Double-walled carbon nanotubes (DWCNTs) can be described as the systems where outer tubes are filled with smaller diameter inner tubes [2]. These carbon nanostructures are the simplest systems for studying the effects of inter-wall coupling on the physical properties of carbon nanotubes.

Other carbon nanostructures attracting much attention in recent time are graphene nanoribbons (GNR) [3]. A possibility of their width and geometry altering is very promising for different applications. Recently GNRs have been formed inside SWCNTs [4]. Forming mechanism of GNRs encapsulated in SWCNTs is a thermal merging of molecules inside SWCNTs. In synthesis of the nanomaterials by SWCNT encapsulation each tube becomes a nano-reactor and the formation of new compounds is performed in clean environment.

In this work different nanosystems formed by SWCNT encapsulation (SWCNTs filled with $FeCp_2$, GNR, DWCNTs) and separated SWCNTs have been studied with optical methods (Raman spectroscopy, optical spectroscopy, photoluminescence) and with an electronic spin resonance technique. We demonstrate the formation of the DWCNTs in initially separated SWCNTs. ESR experiments on M-SC separated SWCNTs and filled with $FeCp_2$ indicated the appearance of two different phases in metallic and semiconducting SWCNTs.

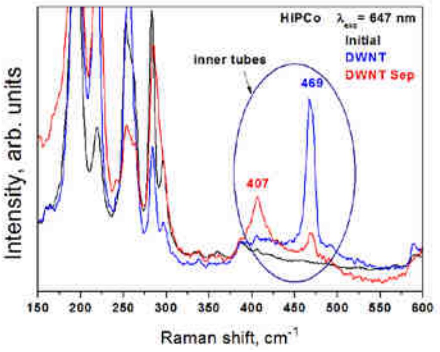

Fig. 1. The Raman spectra of the initial HiPCo material (*black*), DWCNTs formed by transformation of the $FeCp_2$ inside the initial HiPCo SWCNTs (*blue*), DWCNTs formed by transformation of the $FeCp_2$ inside of separated HiPCo SWCNTs (*red*).

*The work was supported by RAS research programs and FP7 IRSES 247007 project.*

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# Raman and coherent phonon spectroscopy of nanotube and graphene

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Raman spectroscopy of single wall carbon nanotubes (SWNTs) and graphene has provided symmetry specific Raman spectra depending on laser energy and the Fermi energy [1,2]. In this talk, we overview our recent works on Raman and coherent phonon spectroscopy of carbon nanotubes and graphene. First, we report theoretical analysis of special Raman spectra which characterize the layer number and stacking order of few layers graphene. Especially, we show how to distinguish ABA and ABC stacking of a tri-layer graphene by Raman spectroscopy [3,4] in which weak Raman spectra at 1690-2150cm$^{-1}$ are relevant to out-of-plane vibrations and thus sensitive the stacking order [5]. In order to assign Raman spectra to combination modes of two phonons, Raman measurement as a function of the Fermi energy is useful in which anomalous behavior of phonon frequency and its spectral width for double resonance Raman spectra was observed as a function of the gate voltage in electro-chemical doping [6]. Finally, we would like to discuss Raman spectra of carbon nanotube using C$^{13}$ isotope in which the phonon spectral width is given as a function of C$^{13}$ concentration, suggesting phonon localization due to the C$^{13}$ isotope [7].

The second topic is coherent phonon (CP) spectroscopy. CP spectroscopy is an alternative way to measure the phonon frequencies, in which (1) ultra short pulse of pump laser light excites the photo-excited carriers, then (2) the photo-excited carriers excite phonons in a coherent way by electron-phonon interaction and (3) we measure the vibration of transmission of the probe light whose the Fourier transformation gives the CP spectra as a function of phonon energy. What is a significant point in CP spectroscopy is that we can directly measure the phase of vibration. According to experiment and calculation, radial breathing mode (RBM) of SWNTs starts either by expanding or shrinking diameter depending on *(n,m)* of a SWNT and the optical transition energy $E_{ii}$ [8]. We investigate the tendency of the RBM phase for more than 20 SWNTs and $E_{ii}$'s. We found that the sign of electron-phonon interaction as a function of the wave vector on the 1D Brillouin zone is essential for determining the initial RBM phases [9]. We will discuss CP spectroscopy of graphene nanoribbon [10].

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# PHOTO-INDUCED INTERACTION BETWEEN ENCAPSULATED PHOTO-ACTIVE MOLECULES AND HOST SINGLE-WALL CARBON NANOTUBES

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Photo-active molecules are confined into single-wall carbon nanotubes to create 1D hybrid systems with new and original opto-electronic properties. This work deals with the encapsulation of oligothiophene and phtalocyanine molecules displaying strong optical absorption in the visible range, respectively around 400 and 670 nm. Encapsulation efficiency is investigated by Transmission Electron Microscopy and spatial resolved Electron Energy Loss Spectroscopy. The physical interaction is mainly investigated by optical spectroscopies. Raman spectra of the hybrid systems exhibit a striking dependence with the excitation energy which is correlated to the optical absorption energy of the photo-active molecule [1,2]. Close to the molecule resonance, the G-band can shift and the Radial Breathing Mode intensities strongly decrease, which suggest a significant photo-induced charge transfer between the photo-active molecules and the nanotubes.

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# AB-INITIO INVESTIGATION OF BAND STRUCTURE OF GRAPHENE NANORIBBONS ENCAPSULATED IN SINGLE-WALL CARBON NANOTUBES

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In this work we ab-initio investigated the band structures of graphene nanoribbons encapsulated in single-wall carbon nanotubes (GNR@SWNT). The calculations have been performed using density functional theory (DFT) with decomposition of electronic wave functions into plane waves as implemented in Quantum Espresso software package [1] and special software developed for this work. The pseudopotential method has been used for some computation. The data have been compared with the results of DFT calculations.

We have used an ultrasoft pseudopotential [2] for the carbon atoms and a plane wave cutoff of 450 eV for the DFT computations.

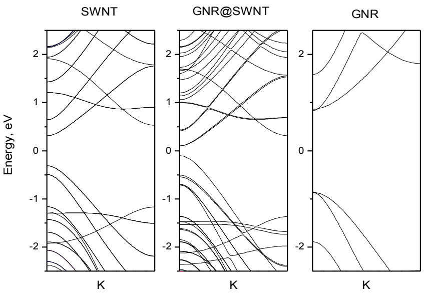

Fig. 1. The calculated band structure of GNR@SWNT

The band structure for different types of GNR@SWNT has been calculated. Figure 1 shows results for the arm-chair nanoribbon with width of 0.74 nm encapsulated in the single-wall carbon nanotube (18,0), the (18,0) nanotube standing alone and the nanoribbon standing alone. The calculations have shown that the band structures of GNR@SWNT looks like a superposition of the band structures of standing alone GNR and SWNT. A weak interaction between GNR and SWNT in such type of structures probably is the reason of this result. Obtained data has a good agreement with the published work [3,4].

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# CARBON NANOTUBES PHOTONICS: PURIFICATION EFFECTS ON NANOTUBE OPTICAL AND ELECTRICAL PROPERTIES

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The use of optics in microelectronic circuits to overcome the limitation of metallic interconnects is more and more considered as a viable solution. Numerous photonic building blocks, compatible with CMOS technology, have been developed. However, integration of all these building blocks on the same chip is a bottleneck, due to the various materials used (Ge, Si, III-V). This drawback could be significantly overcome by considering carbon nanotubes, which have the ability to emit, modulate and detect light in the wavelength range of silicon transparency. That makes them a promising candidate and in consequence an alternative material for active device in silicon photonics technology.

Few years ago, we have developed an efficient method to extract semiconducting nanotube (s-SWNT), using a polyfluorene agent in toluene followed by ultracentrifugation steps [1]. We demonstrated that this method allows obtaining metallic-free s-SWNT samples, as confirmed by photoluminescence, absorption and Raman spectroscopy, and the realisation of high Ion/Ioff FET devices.

This achievements leads to the first experimental demonstration of a strong optical gain of 160 $cm^{-1}$ at a wavelength of 1.3 µm in (8,7) s-SWNT at room temperature [2]. A special emphasis will be put on the s-SWNT extraction, as optical gain could not be achieved in a raw or lowly extracted sample.

Carbon nanotube properties were then relied on the existing silicon photonic platform, and we envision the use of carbon nanotubes as active optoelectronic devices in silicon. A complete study of the coupling between carbon nanotubes and silicon waveguides was performed [3]. In particular, temperature independent emission up to 100°C from carbon nanotubes in silicon was demonstrated, which opens bright perspectives for future high performance integrated circuits.

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# SINGLE-CHIRALITY SEPARATION OF SINGLE-WALL CARBON NANOTUBES BY ONE-STEP GEL CHROMATOGRAPHY

Huaping Liu[1,2], Takeshi Tanaka[1], Yasuko Urabe[1,2], and Hiromichi Kataura[1,2]

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Mixed production of metallic and semiconducting single-wall carbon nanotubes (SWCNTs) with a variety of diameters is one of the most serious problems for their electronic device applications. To solve this problem, we have developed multicolumn gel chromatography method (Fig. 1, left) for the precise structure sorting of semiconducting (S-) SWCNTs using commercially available Sephacryl gel [1]. Appling this method twice to HiPco SWCNTs, we could sort out 13 kinds of S-SWCNTs by the difference in the local C-C bond curvature (Fig. 1, right). However, this two-step separation method is not effective to be applied to the large scale separation. For the further improvements, we have analyzed separation mechanism and then found that it is possible to control the interaction between S-SWCNTs and the Sephacryl gel by changing surfactant concentration and the system temperature. Finally, we succeeded in simplifying the separation procedure and 7 kinds of single chirality S-SWCNTs were obtained by the single step multicolumn method.

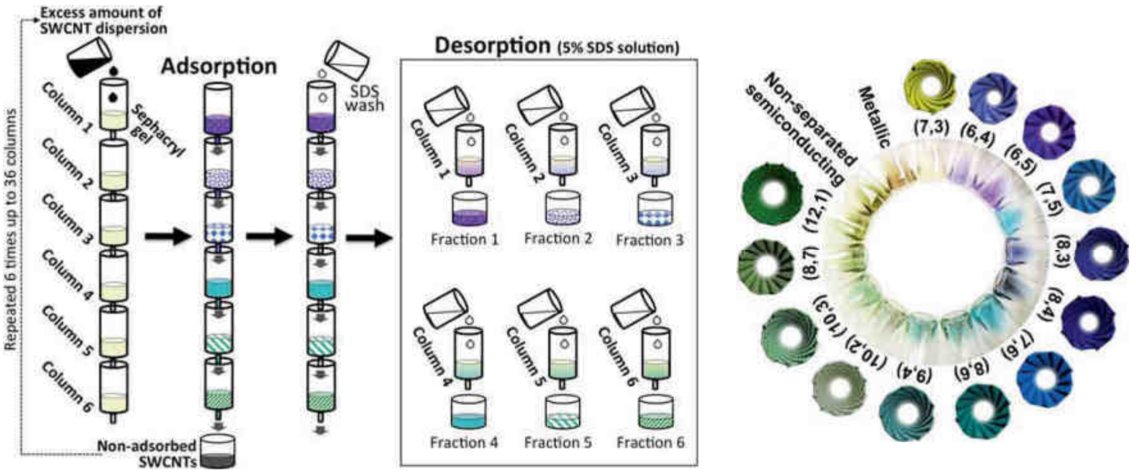

Fig. 1. Left, schematic diagram of a chirality separation of the S-SWCNTs using multicolumn gel chromatography. Right, solutions and molecular structures of 13 chiral S-SWCNTs. [2]

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# COMPLEX OPTICAL STUDY OF CARBON NANOTUBES WITH A NARROW DIAMETER DISTRIBUTION

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Recent progress in a controlled production of carbon nanotubes have allowed developing their applications in electronics, nonlinear optics etc. In our work we used a complex optical diagnostics for the carbon nanotubes samples with a narrow diameter distribution. These nanotubes with close diameters were synthesized on a $Co_xMg_{1-x}O$ solid solution. The $Co_xMg_{1-x}O$ catalyst was prepared by impregnation followed by subsequent calcinations [1]. It is common to use three optical methods (optical absorption spectroscopy, Raman spectroscopy and photoluminescence) to make the overall characterization of the sample.

The electronic parameters of these nanotubes appeared to be measurable with the resonant Raman scattering. Under the different excitation energies the different bands in the Raman spectra (breathing modes, one- or two-phonon scattering) were dominated. This was a consequence of the resonant conditions for outgoing (rather than for incoming) photons. The values of electronic transitions have been estimated on the base of the energy of incoming light and energies of each type of vibrations. The Raman estimations have been confirmed by direct data of UV-vis-NIR optical absorption and Photoluminescence spectroscopy.

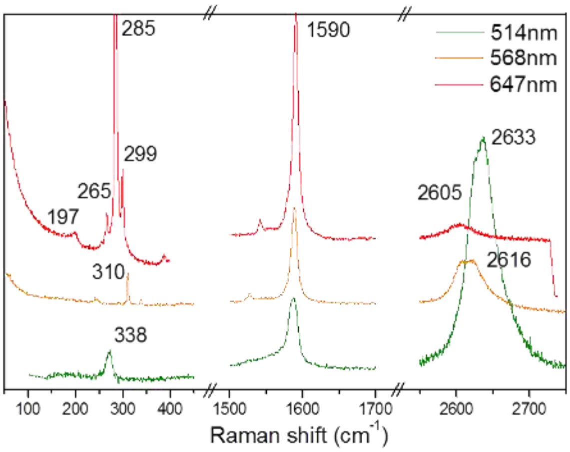

**Fig. 1.** Raman spectra of SWNTs with a narrow diameter distribution taken with different excitation wavelengths.

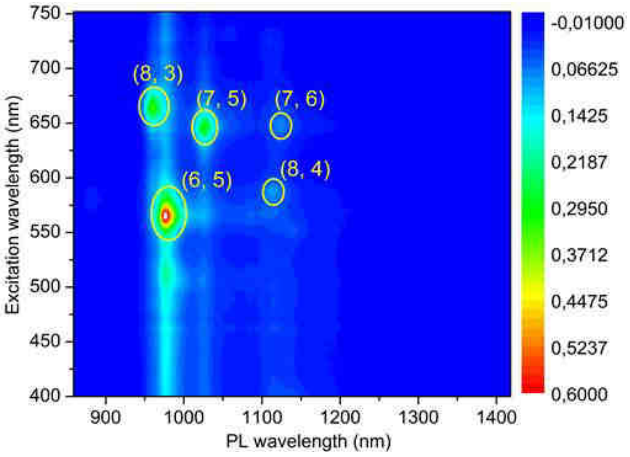

**Fig. 2.** A photoluminescence map of SWNTs with a narrow diameter distribution.

*The work was supported by RFBR-09-02- 00792 and RFBR-11-02-92121 projects and MK-5618.2012.2 grant.*

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# COMPARATIVE STUDY OF REFLECTANCE PROPERTIES OF NANODIAMONDS, $sp^2/sp^3$ COMPOSITES, ONION-LIKE CARBON AND MULTIWALLED CARBON NANOTUBES.

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The ability to adsorb and reflect the EMI makes carbon nanomaterials (nanocarbons) the promising candidates for numerical potential applications related to EMI absorbance in a wide spectral region. Here we have measured diffuse reflectance of nanodiamond (ND), $sp^2/sp^3$ composites, onion-like carbon (OLC) and multiwalled carbon nanotubes (MWNTs) in infrared, visible and UV regions. The diffuse reflectance spectra of these materials are analyzed taking into account the size and defectiveness of graphene sheets which are considered as the main building blocks of $sp^2$-carbon based nanocarbons. We have controlled defectiveness of all nanocarbons with HR TEM, Raman spectroscopy, temperature dependence conductivity and magnetoresistance measurements. The diffuse reflectance of carbon nanomaterials depends mainly on the electronic configuration, defect concentration, size of graphene-like ordered fragments and agglomerates of nanoparticles along with their morphology.

# CARBON NANOTUBE ANTENNA: THEORY AND EXPERIMENTAL DETECTION IN THIN COMPOSITE FILMS

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As indicated by several experimental reports (since 1997), the broad peak in the terahertz and the far-infrared regimes is observed in the conductivity spectrum of composite materials containing single-wall carbon nanotubes (SWNTs). Typically, the peak frequency is located in the range from 50 to 200 cm$^{-1}$. Some research groups have suggested that the localized plasmon (antenna) resonance is responsible for this terahertz conductivity peak (TCP), with central frequency depending on the length of SWNTs. In contrast, other researchers have suggested that the TCP is a result of the interband transition in a small gap induced by the finite radial curvature of SWCNTs. Then transition frequency must depend on the SWNT diameter. As theoretically shown in [1], both effects—the interband transition and the localized plasmon resonance—contribute simultaneously and cause the appearance only one conductivity peak; moreover, at room temperature the contribution of antenna effect prevails.

In the talk we report a theory and optical density measurements carried out on thin films containing either SWCNTs or SWCNT bundles [2]. All samples were prepared by a simple technique that permitted the selection of different SWNT lengths in different samples without significant differences in electronic properties. Fourier-transform infrared spectroscopy showed that the optical-density peak, same as the TCP, shifts to higher frequencies as the SWNT length is reduced. The TCP wave number increased from 150 to 1000 cm$^{-1}$ at room temperature as the SWNT length decreased from 1 to 0.15 μm. The frequency shift of the TCP is attributable to the antenna resonance and is supported well by calculations for a relevant physical model [1].

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# ELECTROMAGNETIC PROPERTIES IN CARBON AND GRAPHENE BASED MONOPERIODIC NANOSTRUCTURES FOR NANOSENSOR SYSTEMS

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Technological interest to contacts of carbon nanotubes (CNTs) or graphene nanoribbons (GNRs) with other conducting elements in a nanocircuit as a basis for effective high-speed nanoelectronics and nanosensors has been the major reason for making calculations of C-Me *interconnect resistances* taking into account the influence of chirality effects in interconnects of single-wall (SW) and multi-wall (MW) CNTs, single-layer (SL) and multi-layer (ML) GNRs with the fitting metals (Me = Ni, Cu, Ag, Pd, Pt, Au) for the predefined carbon system geometry [1].

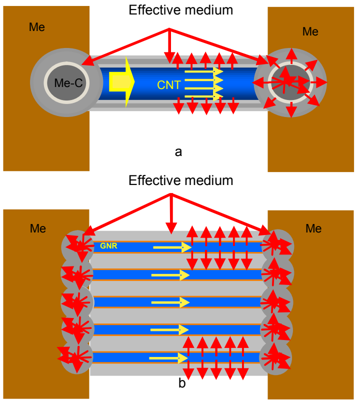

Fig.1. CNT-Me and GNR-Me based models of nanodevices prototypes

The cluster approach based on the multiple scattering theory formalism as well as effective medium approximation (EMA-CPA) can be efficiently used for nano-sized systems modeling. This allows calculating the dispersion law $E(\mathbf{k})$, the electronic density of states, the conductivity, *etc.* taking into account nanoobjects symmetries and and dimensions (quantum dots, nanowires, nanotubes, functionalized nanodevices) [1].

Wide-scale simulation results in *interconnect electromagnetic properties* (interconnect resistances, frequency (GHz, THz) and temperature properties) are presented. Parametric calculations of pure CNT conductivities for various chiralitites are also carried out. The model of CNT growth with the predefined chiralities in a magnetically managed CVD process with the use of magnetically anisotropic $Fe_xPt_{1-x}$ nanoparticles with various substitutional disorders is developed. A special attention is paid to the unique property of interconnects such as the presence of *dangling atomic bonds* that make interconnects chemically, electrically and magnetically sensitive. This property allows considering interconnects as perspective nanosensor structures [2].

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# Tuesday, July 31

# GRAPHENE PHOTONICS AND OPTOELECTRONICS

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The richness of optical and electronic properties of graphene attracts enormous interest. So far, the main focus has been on fundamental physics and electronic devices. However, it has also great potential in photonics and optoelectronics, where the combination of its unique optical and electronic properties can be fully exploited, the absence of a bandgap can be beneficial, and the linear dispersion of the Dirac electrons enables ultra-wide-band tunability[1]. The rise of graphene in photonics and optoelectronics is shown by several recent results, ranging from solar cells and light emitting devices, to touch screens, photodetectors and ultrafast lasers [1]. Despite being a single atom thick, graphene can be optically visualized [2]. Its transmittance can be expressed in terms of the fine structure constant [3]. The linear dispersion of the Dirac electrons enables broadband applications. Saturable absorption is observed as a consequence of Pauli blocking [4,5]. Chemical and physical treatments enable luminescence [1,6]. Graphene-polymer composites prepared using wet chemistry [4-6] can be integrated in a fiber laser cavity, to generate ultrafast pulses, and enable broadband tunability [4,5]. Graphene’s suitability for high-speed photodetection was demonstrated in an optical communication link operating at 10 Gbit $s^{-1}$ [7]. However, the low responsivity of graphene-based photodetectors compared with traditional III-V-based ones is a potential drawback. By combining graphene with plasmonic nanostructures, the efficiency of graphene-based photodetectors can be increased by up to 20 times, because of efficient field concentration in the area of a p-n junction [8]. Additionally, wavelength and polarization selectivity can be achieved by employing nanostructures of different geometries [8]. Light-graphene interaction can be tailored by using microcavities [9]. Photodetection of far-infrared radiation (from hundreds of GHz to a few THz) is important for a variety of potential applications, ranging from medical diagnostics to process control, and homeland security. THz radiation penetrates numerous commonly used dielectric materials, otherwise opaque for visible and mid-IR light. At the same time, it allows spectroscopic identification of hazardous substances and compounds, through their characteristic molecular fingerprints. In this spectral region, due to the unavoidable doping, Pauli blocking does not allow detection exploiting the common photon-induced creation of charge carriers. Efficient THz detection in grapheme can be achieved exploiting the oscillating fields in a graphene field effect transistor [10]. This enables high-sensitivity, room temperature, large-area operation, not limited to a specific region of the THz range [10].

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# Electronic transport in intermediate sized multiwalled carbon nanotubes

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We have measured the low temperature transport properties of single multiwalled carbon nanotubes (MWNT) of diameters (D) in the range 2-10 nm, see fig. 1. Almost all previous work on MWNT’s has been on tubes with diameters above 10 nm. In nearly all samples in this work, with D < 10 nm, the gate dependent conductance (fig. 1, right) exhibits a gap whose size increases with the inverse tube diameter and increasing electrode separation. This so called transport gap is attributed, based on the experimental findings, on a combination of localization effects and narrow diameter induced gaps in the electronic band structure.

These results have significant similarities to the current research on graphene nanoribbons (GRN). As graphene does not intrinsically possess a bandgap, GNR’s are fabricated, where a gap is created via quantum confinement due to the narrow width of the channel/nanoribbon. The size of the gap is then roughly in a similar inverse relation with the width of the constriction as in the case of the diameter dependence of the MWNT's in our work.

The transport gap has not generally been observed in the previous works on MWNT’s because of the large diameters of the tubes in these. Our work, of which some early results were published previously [1], complements and bridges previous works on both single walled nanotubes and MWNT’s, and also to the field of GNR’s.

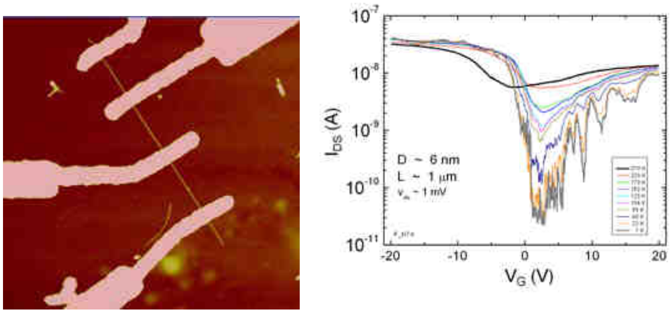

Figure 1. Left: AFM image of a MWNT contacted with four electrodes. Right: Current vs. gate voltage for a MWNT at different temperatures between 270 K and 7 K.

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# COMBINING DIFFERENT MEASUREMENTS ON INDIVIDUAL CARBON NANOTUBES

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We have studied the individual properties of freely suspended carbon nanotubes (CNTs) with fully clear optical path. Such sample geometry allows us using three different measurement routes: electronic transport measurements, optical spectroscopy and electron diffraction (ED) measurements.

The two latter techniques give two independent methods to determine the chirality of the nanotube [1,2]. CNTs with determined chiral indices are then studied, allowing us to tie the optical and electronic response to a known lattice structure. We have e.g. recently performed time-resolved (femtosecond) four-wave-mixing (FWM) measurements on individual CNTs [3], directly probing both exitonic and vibrational dynamics. Also first second harmonic imaging from individual CNTs are demonstrated [4].

We will present those measurement, as well as transport and Raman measurements of known individual CNTs down to cryogenic temperatures.

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# PHOTOCURRENTS IN GRAPHENE AND CARBON NANOTUBES

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In my talk, I overview experimental and theoretical investigations of photogalvanic effects in graphene and carbon nanotubes. The following effects are planned to be discussed.

1. The photon drag effect observed in single-layer graphene under oblique incidence of the laser light, in the terahertz and infrared frequency regions [1,2]. For the terahertz radiation the photon drag effect can be considered as a dynamic Hall effect. The special attention is paid to the circular drag photocurrent dependent on the radiation helicity and inverting its polarity under reversal of the circular polarization.
2. Terahertz radiation driven chiral edge currents which are excited in single-layer graphene samples by illuminating the graphene edges with circularly polarized radiation at normal incidence [3].
3. Pure valley currents induced by the homogeneous normal-incidence photoexcitation of graphene [4]. The intravalley current appears because of the reduced symmetry $D_{3h}$ of the valleys $K$ and $K'$, while the net electric current is forbidden by the overall $D_{6h}$ point-group symmetry of graphene.
4. Photogalvanic properties of graphene superlattices (SLs) formed by periodic strain [5]. Asymmetric graphene SLs belong to the class of quantum ratchets and allow helicity-dependent photocurrents under normal incidence of radiation.
5. Effects inherent for chiral carbon nanotubes: circular photogalvanic effect (PGE), magneto-induced linear PGE, natural circular dichroism, magneto-spatial dispersion of light absorption, magneto-chiral *dc* electric current quadratic in the bias voltage applied to a chiral nanotube [6, 7].

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# GATE-TUNABE TUNNELING TRANSPORT IN BILAYER GRAPHENE

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We present a review of our experiments on graphene transistors in its potential use as atomic film switching devices.

We found that large transport energy gaps (>100 meV) can be fulfilled in dualgated bilayer graphene underneath a simple alumina passivation top gate stack, which directly contacts the graphene channels without an inserted buffer layer. With the presence of energy gaps, the electrical properties of the graphene transistors are significantly enhanced, as manifested by enhanced on/off current ratio, subthreshold slope, and current saturation. For the first time, complementary-like semiconducting logic graphene inverters are demonstrated that show a large improvement over their metallic counterparts.

We also demonstrated a tunneling and rectification behavior in bilayer graphene with bandgap (Fig.1). A stepped dielectric top gate creates a spatially modulated electric field, which opened the band gap in the graphene and produced an insulating region at the p–n interface. Furthermore, series of tunneling junctions enabled unipolar graphene transistors.

This result may open the way for logic applications of gap-engineered graphene.

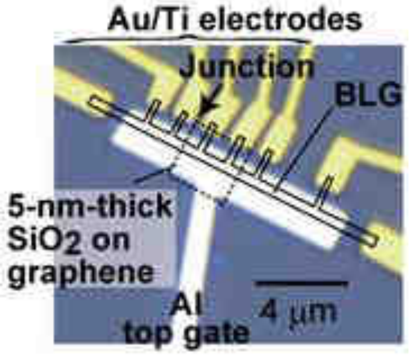

Fig.1 Optical-microscope image of gate-tunable bilayer graphene transistor.

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# ALL-OPTICAL CONTROL OF PHOTOCURRENTS IN GRAPHENE

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Owing to a gapless linear band structure and high mobility of massless charge carriers, graphene is considered as a material of future all-wavelength optoelectronics. Recent advances in graphene synthesis and, especially, in the CVD provide production of high quality samples suitable for manufacturing optical and optoelectronic devices. Number of approaches has been proposed to utilize optically/THz excited carriers, whose ultrafast dynamics is still under debate, for electronics. However, most of these approaches require modification of the graphene electronic structure by biasing the sample or introducing a built-in potential at the metal-graphene or graphene-graphene contacts [1]. Another approach suggests injection and coherent control of ballistic photocurrents using third-order nonlinear processes such as quantum interference of one- and two-photon absorption pathways and frequency mixing [2].

We present an alternative all-optical technique to inject the ultrafast currents in unbiased graphene. The proposed method is solely based on a second-order nonlinear effects and therefore provides substantially higher efficiency then latter. In the experiment, we make use of extremely efficient photon-drag effect in graphene, which manifests itself as transfer of the photon momentum to hot electrons during the one-photon interband absorption in graphene [3,4]. The irradiation with intensive linearly polarized femtosecond as well as nanosecond laser pulses in VIS-IR spectral range induces transient picosecond currents in the graphene. The direction and amplitude of the injected currents are completely driven by the orientation of the polarization plane azimuth, angle of incidence and intensity of the pump beam. Moreover, we experimentally demonstrate the possibility of all-optical control of the injected currents by introduction another laser pulse, which incidents at mirror-reflection direction of the first one (Fig.1). In this experimental configuration, the currents injected into graphene are fully driven by the ratio of the pump pulse intensities and mutual orientation of their polarizations. The obtained results give new insight on the hot carrier dynamics in graphene, while the opportunity of all-optical control of the transient currents may be implemented in novel optoelectronic and THz devices.

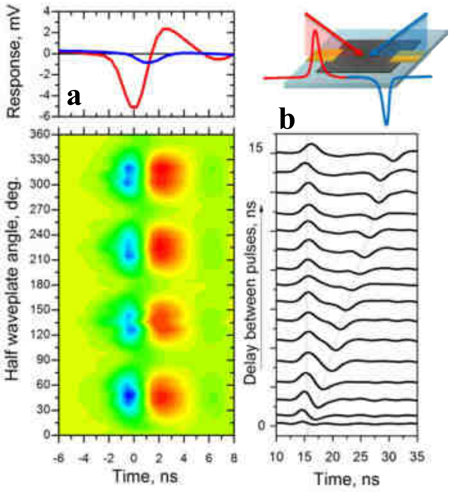

Fig. 1 a) Waveforms and polarization dependence; b) two-beams control of the injected currents.

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# COMBINED PHOTONIC CRYSTALS AND GRAPHENE FOR LIGHT HARNESSING

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Inside the wide family of periodic photonic structures, dielectric photonic crystals have played a fast growing part during the last 25 years, their specificity inherently lying in the high index contrast of the periodic modulation (generally more than 200%) introduced in the optical medium. The concept of three dimensional photonic crystal (3D PhC) was simultaneously introduced by S. John [1] and E. Yablonovitch [2]: it is currently considered as a must for 3D spatial and temporal confinement of the light. In practice the fabrication of 3D PhCs is very difficult, and most of the developments have concerned the production of 1D and 2D PhCs formed in wave-guiding dielectric slabs. These high-index-contrast periodic structures can indeed be fabricated using planar technological approaches that are familiar to the world of integrated optics and microelectronics. They consist practically in 1D or 2D structuring of a planar dielectric/semiconductor membrane waveguide, where photons are “index guided”, that is to say vertically confined by the profile of the optical index. In most of the reported works, 1D-2D PhCs are meant to operate solely in the 2D wave-guiding configuration and, hence, are limited to a 2D control of photon trajectory: in this context, they have been the matter of an innumerable number of reports, publications, conferences and tutorials. In the present tutorial, we will not therefore contribute further to this abundant literature and will not talk about 2D PhCs operation, where control of light is restricted to the sole in plane wave-guiding configuration. We will instead concentrate on more recent developments where use is made of 1D-2D PhC membranes for efficient 3D harnessing of light, along a variety of configurations including both in plane wave-guided and free space radiated regimes and where the basic building block of devices consists in a surface-addressable resonant PhC membrane structure.

The physical principles of surface-addressable resonant PhC membrane structures will be presented in detail: they are based on the resonant coupling of incoming optical beam (radiated mode) with wave-guided Bloch modes in the PC membrane, which may occur whenever wavelength and *k*-vector matching conditions are met. The essential driving forces and controlling parameters will be described and routes for simple design rules, resulting in the production of structures endowed with the desired characteristics in the space-time domain will be given. Exemplifying use of surface-addressable resonant PhC membrane structures in a variety of devices will be presented [3].

The richness of optical and electronic properties of graphene is currently attracting enormous interest. A considerable potential lies in photonics and optoelectronics, where the combination of its unique optical and electronic properties can be fully exploited [4]: for example, the linear dispersion of the Dirac electrons in graphene is the distinctive feature which makes this material ideal for wide spectral bandwidth (from 0,4 μm up to middle and far infrared) and ultra-fast saturable light absorption. Also, it has been recently demonstrated that graphene possesses a very large $3^{rd}$ order non-linear coefficient ($\chi3$). In addition, a major asset of graphene lies in the fact that its remarkable photonic properties can be easily tuned by shifting the Fermi level around the Dirac singularity, where the density of electronic states is rather low. In this presentation, we further argue that the exceptional photonic properties of graphene can be further magnified if the material is combined with surface-addressable resonant PhC membrane structures, taking advantage of their remarkable photonic confining properties. In particular it is shown that the heterogeneous planar integration of graphene with silicon on insulator PhC membrane structures provides an ideal generic platform for this purpose.

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# NANOCARBON IN ORGANIC SOLAR CELLS

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Organic solar cells promise a beneficial combination of efficiency, lifetime, and cost so that they are expected to compete with inorganic solar cells in the nearest future. The most attractive in organic solar cells is that they can be lightweight, flexible, easy compatible with roll-to-roll technologies and, hence, be cheap. The efficiency of organic solar cells has been essentially increased for the last year, and the key milestone in power conversion efficiency of 10% has been reached [1].

Fullerenes are indispensible components of the state-of-the-art organic solar cells, and they are used as an electron acceptor in heterojunction solar cells. Moreover, other nanocarbon materials are promising for organic solar cells, e.g., graphenes can be used as thin-film transparent electrode materials. In this talk, recent achievements in nanocarbon materials for organic solar cells are presented and future trends are discussed.

We start with formulation of basic requirements for organic solar cell materials in terms of their electronic, optical and physicochemical properties, and then analyse fullerenes, nanotubes and graphenes. The main focus of the talk is on fullerene derivatives. The drawbacks of pristine fullerenes ($C_{60}$ and $C_{70}$) as solution-processed materials for solar cells are their low absorption of solar radiation, too high electron affinity, and low solubility. Because of this $C_{60}$ and $C_{70}$ are functionalized to neutralize these drawbacks. Surprisingly, despite active research, the best fullerene derivative for solution-processed organic solar cells is so-called PCBM ([6,6]-phenyl-C61-butyric acid methyl ester or its $C_{70}$ analog) synthesized 17 years ago [2]. PCBM is appeared to have optimal solubility in organic solvents, but its optical absorption and LUMO energy are too low that limits the photocurrent and the voltage of heterojunction solar cells, respectively. We analyse resent studies on methanofullerenes for solar cells and present our results on the novel type of methanofullerenes, indolinone-substituted methanofullerenes [3]. To decrease the fullerene LUMO energy, fullerenes complexes with metals can be used. Our recent studies on exohedral metal complexes of $C_{60}$ are presented. The possible ways of fullerene functionalization are discussed.

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# GIANT THERMAL RADIATIVE HEAT TRANSFER THROUGH GAPS FILLED WITH CARBON NANOTUBES

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Effect of a strong enhancement of a thermal radiative heat transfer between closely spaced bodies was predicted by Rytov [1]. In the presence of another body in the near vicinity of the hot surface the well-known photon tunneling phenomenon arises between two surfaces which leads to the dramatic increase of the heat transfer compared to the value restricted by the back-body limit. In other words, not only propagating waves but evanescent ones also carry electromagnetic energy between two surfaces. However, in the mid-infrared range it practically holds only when the gap between two media is as small as a few tens of nanometers.

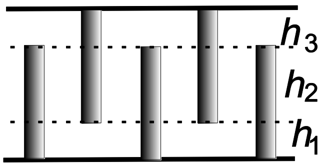

Fig. 1. Arrangement of CNTs.

We suggest to fill in the gap between bodies with a metamaterial which transforms the evanescent spatial spectrum into propagating one [2]. Metamaterials performing this manipulation with electromagnetic waves possess hyperbolic dispersion. For the infrared range such metamaterials can be realized as arrays of aligned carbon nanotubes (CNT) or metal nanowires. An advantage of the CNT array is its capability to support propagating waves for even very large transversal components of the wave vector $k_x$ in ultra-broadband frequency range [3].

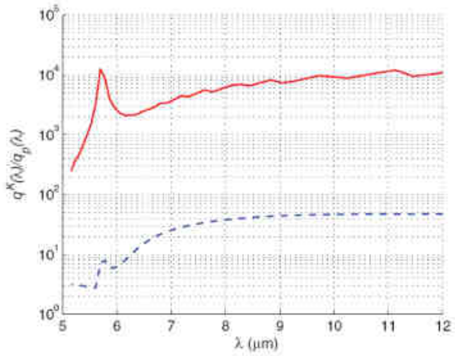

Fig. 2. Ratio of the total spectral density of the transferred heat $q^K(\lambda)$, to the spectral density of heat, transferred by propagating waves only $q^P(\lambda)$. Logarithmic scale.

Fig. 1 shows a possible scheme of arrangements of nanotubes between the bodies. The inter-digital arrangement prevents direct heat transfer via phonons, providing propagation of electromagnetic waves for large $k_x$. Fig. 2 illustrates enhancement of the radiation heat transfer through the micron gap, carried by carbon nanotubes (red), compared to transferred through vacuum gap (blue). $K$ is the upper limit of integration over $k_x$. Even integration over a half of the first Brillouin zone of the CNT array lattice shows a three-order enhancement of the radiative heat transfer. This effect will take place within a frequency range containing the most radiating thermal energy.

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# 3D GRAPHENE-BASED STRUCTURES: FORMATION, PROPERTIES, AND POTENTIAL APPLICATIONS

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The 3D graphene-semiconductor nanoshells were fabricated using the technology of [1-2] that was used in many countries for forming unique precise semiconductor and metal solid nanoshells [3-5] substantially differing in their properties from planar films [6] and having many applications ranging from tubular lasers, мetamaterials, and sensors to nanorobotic.

Test samples of various graphene devices designed around such shells, including precise arrays of hybrid graphene-semiconductor field emitters [7]. It should be noted here that the technology of hybrid graphene-semiconductor shells enables fabrication of true out-of-plane elements, and it can be scaled to allow full-wafer processing in a parallel fashion.

Control of local buckling and bending in graphene-semiconductor films, and also controlled generation of elastic strains in graphene, provide a new engineering approach suitable for design of strain-based nanodevices. We numerically investigated 3D shapes obtained by local buckling of a graphene layer covering a strained InGaAs bilayer film on a GaAs substrate [8]. Such 3D shapes have potential in forming graphene-based quantum devices and biomedical instruments [9].

It is shown that, unlike planar graphene layers, graphene-based nanoshells exhibit unusual ballistic-transport properties and giant gradient phenomena.

In the second part of the report, we discuss some extraordinary properties of multigraphene layers comparable in thickness with Debye screening length in transverse direction. Surprising properties of functionalized multigraphene are outlined. For instance, we found that the current response of multigraphene to ammonia adsorption was strongly dependent on multigraphene thickness, and it exceeded the current response demonstrated by single-layer graphene by up to seven orders of magnitude [10]. We found that multigraphene intercalated with compounds experiences a sharp thermally stimulated semimetal-dielectric transition enabling fabrication of 3D functionalized structures with unique properties. Results on the formation, with the help of imprint nanolithography (Eitre 6 “Obducat”), of new graphene nanostructures, including metamaterials, moiré structures and structures intended for investigation of plasmon effects, are demonstrate.

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# ELECTROLUMINESCENCE OF CDS AND CU:CDS NANOPARTICLES GROWN ON ALIGNED CARBON NANOTUBES

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Electroluminescence properties of cadmium sulphide (CdS) nanoparticles and those doped with copper (Cu:CdS) were studied in the conditions of field electron emission from multiwalled carbon nanotubes (CNTs) used as template for nucleation and growth of nanoparticles. CdS nanoparticles have been grown on the surface of aligned CNT array using a chemical bath deposition method [1]. Cu inserting into CdS crystal lattice was achieved adding certain quantity of $CuCl_2$ in water solution of $CdCl_2$, thiourea $(NH_2)_2CS$, and ammonia $NH_3$. The size, crystal ordering, and surface composition of nanoparticles was shown to depend on the solution temperature, synthesis duration, and defectness of CNT walls. It was found that CdS nanoparticles are formed on the surface of as-prepared CNTs during 2 minutes at room temperature, while at least 5 minutes are required for growth of CdS nanoparticles on the CNTs, annealed at 1000°C in an argon flow. The observed easer formation of CdS nanoparticles on poor graphitized CNT walls was explained based on density functional calculations of the interaction of Cd(II) complexes with perfect and defective graphitic fragments.

Electroluminescence was investigated on a vacuum set-up. Substrate with vertically oriented CNTs decorated with CdS nanoparticles was located on a negative electrode, while an ITO (indium tin oxide) coated glass was used as an anode. Photographs of glow of CdS/CNT cathode were taken through a transparent window in the measuring cell. It was found that CdS nanoparticles became luminescent during the field electron emission from CNTs. [2]. Efficiency of the electroluminescence depends on the CdS crystallinity and size. The large well-crystallized nanoparticles give the bright spots on the cathode image, while the glow from smaller, poor ordering nanocrystalls are strongly scattered. Appearance of red and orange spots was attributed to impurities on the CdS surface. We showed that color of the luminescence dots changes in blue with copper doping of CdS nanoparticles (Fig. 1).

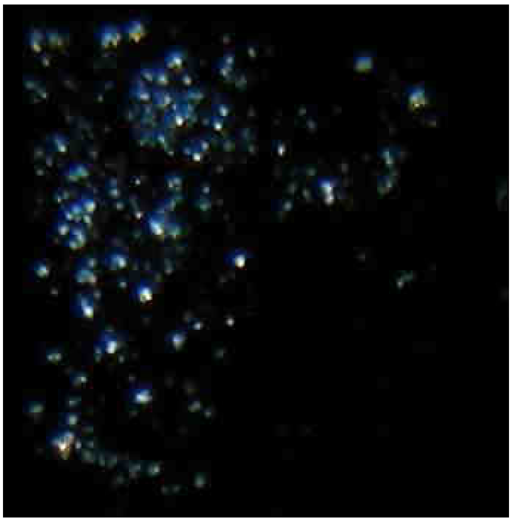

Fig. 1. Image of surface glow of Cu:CdS/CNT cathode

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# NONLINEAR LIGHT SCATTERING IN NANOCARBON SUSPENSIONS

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The light scattering is one of the most spectacular phenomena of nature. The knowledge of the new laws of light scattering is important for optical devices design. The study of the light scattering in nanocarbon suspensions is of practical interest for developing of optical limiters, laser pulse duration controllers and light polarization analyzers.

It has been recently demonstrated a possibility of continuously controlling the duration of the nanosecond laser pulses by the method of *z*-scanning of a cell containing carbon nanotube (CNT) suspension [1, 2]. The shortening of the duration of pulses of a passively Q-switched laser with protracted trailing edges is accompanied by symmetrization of the time profile of pulses. This phenomenon results from nonlinear scattering with the optical limiting (OL). The similar results have been obtained in aqueous suspension of nanodiamonds (ND). And the employment of the aqueous suspension of ND for this purpose is more preferable because of its overstability to the high power laser action. Therefore NDs are more suitable as the optical limiters of high laser power too.

The shape and the energy $e_s^{90}$ of the $90^0$-scattered laser pulses were studied as a function of the input fluence under the OL in CNT and ND suspensions. The shape, the duration and the time shift of the $90^0$-scattered laser pulses are intricate functions of the input fluence. The power density as a function of $e_s^{90}$ consists of the linear and nonlinear terms. The nonlinear term cannot be described by the well known nonlinear phenomena. The obtained data are interpreted by the thermally induced nonlinear and Rayleigh, Mie and Tyndall scattering processes with high and low input fluencies, respectively.

The influence of the nanoparticle $C$ concentration and laser $\Phi$ polarization angle on nonlinear light scattering was investigated in relation to their OL behavior both in the CNT and the ND suspension for laser pulses with 17 ns duration and wavelength of 532 nm. It was shown that limiting threshold does not depend on $\Phi$, while the $\varepsilon_s^{90}$ is described by the $(a+b\sin^2\Phi)$ - law, where $a$, $b$ are the coefficients depending on the incident power density. We showed that $\varepsilon_s^{90}$ is a complicated function of $C$. Finally, it was shown that at 532nm the major mechanism of OL in fullerenes aqueous suspension is nonlinear refraction and nonlinear absorption. The contribution of the nonlinear scattering to the OL in this suspension is negligible.

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# Poster session I

# SYNTHESIS OF MULTI-LAYER GRAPHENE FILMS ON NICKEL SURFACES

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Graphene consists of one layer of carbon atoms arranged in hexagons in two-dimensions. Graphene has the unique electronic and optical properties. It absorbs 2.3% of intensity of the incident light over a wide spectral range and demonstrates a high charge mobility even at room temperature. This makes graphene a promising material for use in various applications.

The single-layer graphene films are required for electronic applications. Sometimes the absorbance of 2.3% could be not enough for the optical applications, for instance, for realization of the mode locking regime in fiber lasers. In this case there is a necessity to use the thicker graphene film (with a number of layers up to 10 or even 20). Thereby a precise control is needed for the number of layers during the synthesis of graphene films.

Using a chemical vapor deposition on the nickel foil from a gas mixture of methane and hydrogen we can obtain graphene films of the variable thickness [1]. It is necessary to follow the main process parameters: a pressure in the chamber, a concentration of the methane in a gas mixture, a maximum temperature of the substrate during the synthesis and the cooling rate.

The most important parameter appeared to be the maximum growth temperature of the substrate during the synthesis. This temperature strongly influences on the thickness of the graphene film (Fig.1). The carbon atoms start to diffuse into the substrate when the temperature exceeds 650°C. The number of penetrated atoms depends on the substrate temperature. The thickness of graphene films depends on the number of carbon atoms pushed out to the surface during the cooling down to the room temperature.
The synthesized samples were characterized by the optical absorption spectroscopy.

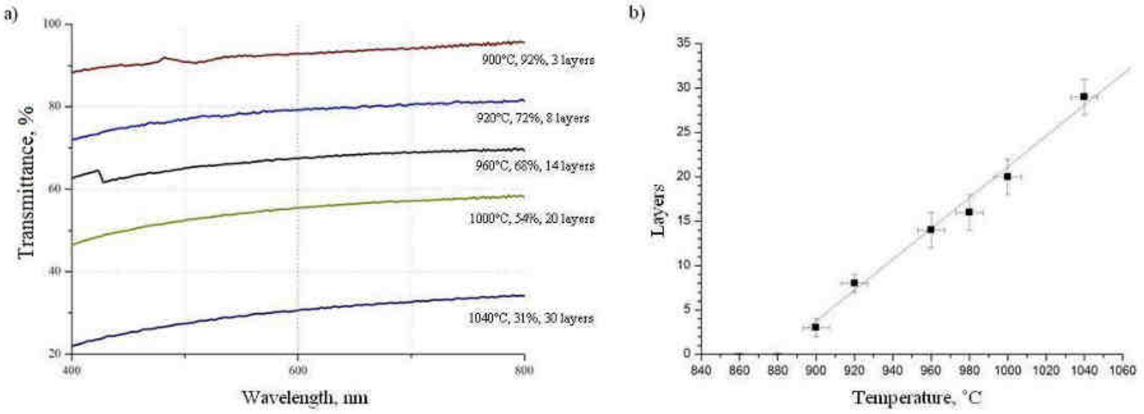

Fig. 1. a) The optical transmission spectra of graphene samples grown at different temperatures, b) a dependence of the numbers of layers on the temperature.

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# N-TYPE SWCNT THIN FILM TRANSISTORS USING MOLECULAR ENCAPSULATIONS TOWARDS HIGH SPEED LOGIC DEVICES

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Because of extremely low effective electrons mass in single wall carbon nanotubes (SWCNTs), semiconducting SWCNTs (s-SWCNTs) can be used as high-mobility channels of thin film transistors (TFTs). For the fabrication of complementary TFTs as a building block of logic circuits, furthermore, carrier control of s-SWCNT is essential. It is known that the p-type TFT can be easily obtained by hole injection from ambient oxygen molecules adsorbed on to the s-SWCNT wall. However, it is not easy to get air stable n-type TFTs.

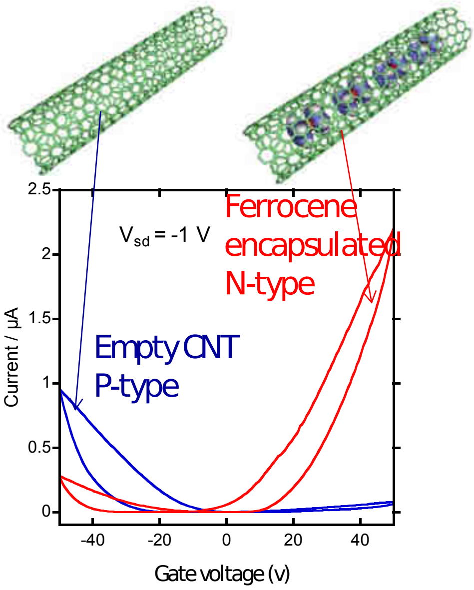

Fig. 1. Transport characteristics of empty and ferrocene filled SWCNT TFTs.

In this work, we prepared ferrocene encapsulated s-SWCNTs using high-purity s-SWCNTs obtained by gel column chromatography method [1] and then used them as n-type channel. Where, high-yield filling of ferrocene molecules and accompanying electron injection was confirmed by Raman, optical absorption, and photoluminescence spectra. In the case of HiPco SWCNTs, smallness of mean diameter probably limited the filling of ferrocene and the filling yield was not good enough to get n-type behaviour of the TFT. We tried to separate the ferrocene filled SWCNTs from the mixture of empty and filled SWCNTs using gel column chromatography. Finally, we successfully obtained highly ferrocene filled s-SWCNTs and then TFTs were fabricated. Figure 1 shows typical transport characteristics of back-gated TFTs. TFT using ferrocene filled s-SWCNTs clearly exhibited n-type behaviours while TFT using empty s-SWCNTs showed normal p-type behaviour. To our knowledge, this result is the first evidence that molecular encapsulating s-SWCNTs can be used as an n-type channel.

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# TOWARDS AN INTEGRATED MODE-LOCKED MICROLASER BASED ON TWO-DIMENSIONAL PHOTONIC CRYSTALS AND GRAPHENE

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Graphene is a well-known carbon nanomaterial with useful electronic and optical properties. It has already been applied as a saturable absorber for self mode-locking regimes in ultra-fast fiber lasers [1,2]. Its combination with a photonic crystal (PhC) [3] could lead to the creation of integrated nonlinear optical devices or pulsed microlasers. This is a new prospective area, which is still poorly studied. In this work, we describe the design, fabrication and photoluminescence (PL) measurements of a III-V based PhC, which could be used as a basis for an integrated mode-locked PhC microlaser with a graphene saturable absorber.

Our 2D PhC is a structure with a sub-micron scale periodic refractive index, which exhibits a photonic bandgap around 1.5um. By creating defects in the lattice, i.e. omitting some air holes (Fig. 1.), we can produce an optical cavity. We use InGaAs/InP quantum wells (QWs) as the active medium emitting around 1.5um. The device is compact (about 10-15um) and works at room temperature. The InP membrane including the QWs is bonded onto a $SiO_2$/Si substrate for improving the laser heat dissipation. The fabrication process of the PhC included e-beam lithography and reactive ion etching. We made various structures with different lattice parameters and cavity lengths for optimizing the coupling between the active medium and the cavity resonances. For the device characterization, we made micro-PL measurements, via exciting the active medium with a pump laser diode at 780nm (CW) coupled vertically, from the top of the sample. The device optical response was collected from the same direction and with the same objective (x50).

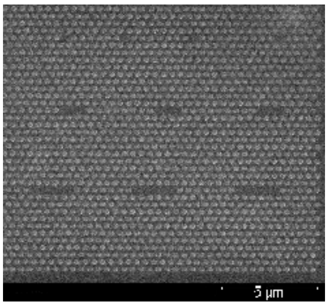

Fig. 1. A SEM image of the fabricated structure including several cavity size.

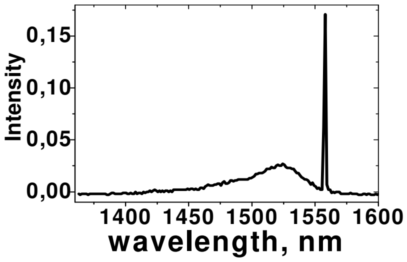

Fig. 2. The photoluminescence spectra from the area of crystal with 5 missing holes. The weak wide band corresponds to the active material emission, the sharp peak is due to the cavity.

The structure shows a wide PL peak between 1460nm and 1570nm, corresponding to the QW emission (Fig. 2.). Lasing in the range of 1504-1558nm with a threshold of about 70uW was observed for several cavities defined by 5 missing holes (Fig.1).

This work represents a first step towards the creation of a microlaser generating a train of short optical pulses. By optimizing the cavity design, and covering locally the PhC with graphene, we expect to exploit the latter as a saturable absorber, key to mode-locking operation.

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# OPTICAL LIMITING IN NANODIAMOND SUSPENSIONS

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Optical limiting (OL) is nonlinear optical phenomenon, which manifests itself as sharp increase of the optical losses when the light intensity in the material overcomes a threshold value. The materials possessing the OL property are of significant interest for the eye and sensor protection as well as for high-intensity optics [1]. We report on the OL in aqueous suspensions of nanodiamonds (ND) and on the dependence of the OL properties on the ND cluster size.

In the experiment, we employed superstable suspensions of ND clusters, which were obtained from detonation nanodiamonds with a modified surface [2]. We studied three suspensions with size of ND clusters of 50, 110 and 320 nm. Figure 1 shows the OL performance of these ND suspensions at the wavelength of 532 nm.

One can observe from Fig.1 that there is no OL in distilled water, i. e. $W_{in}/W_{out}$ = const, where $W_{in}$ and $W_{out}$ are input and output fluences. However in the ND suspensions, the increasing of $W_{in}$ results in OL, i. e. $W_{out}$ as a function of $W_{in}$ shows saturation. The saturation value of the output fluence strongly depends on the ND cluster size. For suspensions with average clusters size of 50 nm, 110 nm and 320 nm the saturation values are 2 J/cm$^2$, 0.7 J/cm$^2$ and 0.35 J/cm$^2$, while the OL thresholds are 2.1 J/cm$^2$, 1.3 J/cm$^2$ and 0.6 J/cm$^2$, respectively. That is the bigger ND cluster size, the higher performance of the suspension in the OL.

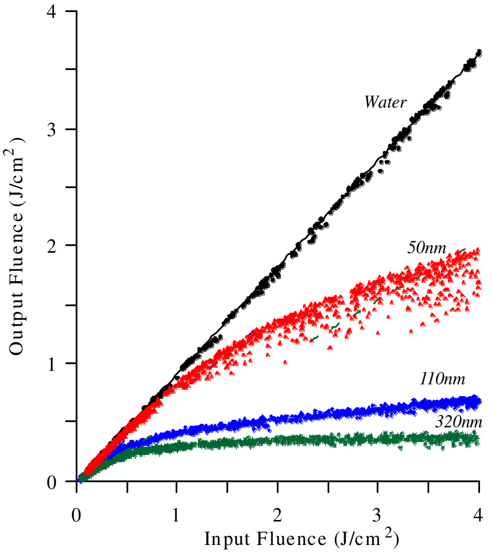

Fig. 1. Output fluence as a function of input fluence in distilled water (black) and ND suspensions with average cluster size of 50nm(red), 110nm (blue) and 320nm (green). The measurements were performed at wave-length of 532 nm and pulse duration of 17 ns.

Our analysis shows that nonlinear scattering is dominating OL mechanism in ND suspension, while the contribution of nonlinear absorption to the reduction of the transmission coefficient is about 25%.

In conclusion, we demonstrate that aqueous ND suspensions show excellent OL performance and hence are promising materials for manufacturing devices for eye and sensor protection from intense laser radiation.

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# DISPERSIONS OF SINGLE WALL CARBON NANOTUBES IN AQUEOUS-ORGANIC MEDIA: EFFECTS OF COMPOSITION AND STRUCTURE ON THE THERMAL AND TEMPORAL STABILITY AND OPTICAL POWER LIMITING PROPERTIES

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Working out a practical material for optical power limiting (OPL) requires rendering its physical properties germane to the conditions of its application and getting optimal set of the OPL parameters (limiting threshold and limiting factor). For the moment suspensions of single wall carbon nanotubes (SWCNT) stabilized by amphiphiles are among the most superior candidates with relevant OPL parameters. To procure their stability spanning a broad temperature interval, including sub-zero values, we focused at aqueous solutions of anti-freezers as dispersing media.

In first place, we studied the critical micellar concentrations and Krafft boundaries of a number of common amphiphiles: sodium dodecylsulfate (SDS), sodium dodecylbenzenesulfonate (SDBS), a blend of SDS with an ionic liquid (IL) hexylmethylimidazolium chloride in a binary eutectic mixture water+glycerol. Sizes, surface charges and composition of micelles were calculated using a molecular-based model of Gibbs energy of aggregation. These data are correlated with optical absorption spectra of SWCNT dispersions in such a medium with the said amphiphilic agents as dispersants. The spectra were monitored over a year's time, the storage being accompanied with cooling of dispersions down to -40 $^{o}$C. These observations showed thermal and temporal stability of all of the suspensions.

OPL properties of the suspensions were tested in a confocal telescopic system in a one-shot and pulse periodic (10 Hz) regimes of laser light (pulse duration 7 ns, wavelength 532 nm). Certain inferences are done regarding the impact of caloric and viscous properties of the medium, on the one hand, and dynamic dielectric functions of the SWCNT's amphiphile microenvironment and its aggregative vs. adsorption properties in a binary polar solvent, on the other, on manifestations of non-linear OPL properties.

We also verified the impact of bundles presence in the system on OPL properties. To this end we processed dispersions with various duration of the ultra-sound treatment (ca 100 Wt): from 5 min to 3 h, conditions of ultracentrifugation being the same ($1.8 \times 10^6$g, duration 1 h). The OPL parameters turned up the best (limiting factor ca 1000) in case of short sonication times (thereby higher content of bundles).

This work was supported by Russian Foundation for Basic Research (grants # 11-03-01106-a, #11-03-00115-a) and St.Petersburg State University ( grant # 12.37.127.2011).

# PHOTOVOLTAIC EFFECT IN NANOGRAPHITE FILMS AT LOW TEMPERATURES

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We have recently demonstrated that CVD nanographite films (NGF) [1] can be used for detection of the nanosecond laser pulses at the temperature as high as 500°C [2]. Here we report recent investigation of the light-induced electric currents generation in NGF at low temperatures from 86 K to 300 K.

In our experiments the copper electrodes were attached to the surface of the NGF film grown on a silicon wafer substrate. The wafer with the film on a special copper holder was placed in a vacuum chamber and cooled down by using liquid nitrogen. The film was irradiated by linear-polarized laser pulses of the Q-switched YAG:Nd$^{3+}$-laser (pulse duration – 20 ns, pulse energy – 1 mJ) and the voltage generated between the electrodes was registered by a digital oscilloscope. The interelectrode dc resistance *R* was measured over the whole temperature range.

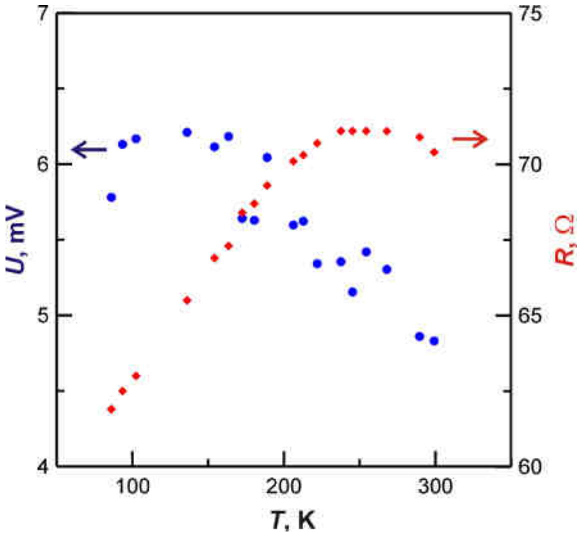

Fig. 1. Temperature dependences of the light-induced potential difference between the electrodes and NGF resistance

We found that the temperature dependence of the light-induced potential difference between the electrodes, *U,* and resistance, *R,* is inverse. One can observe from Fig. 1 that the interelectrode resistance decreases when the temperature decreases, while the photogenerated voltage grows. Specifically, the decrease of the film temperature from 300 K down to 86 K was accompanied by the 15% photovoltage growth and the reduction of the resistance from 70 Ω to 62 Ω.

The results obtained are discussed in terms of the surface photogalvanic effect and photon-drag effect.

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# PHOTOVOLTAIC CHARACTERISTICS OF MULTIWALL CARBON NANOTUBE/SILICON HYBRIDS PRODUCED USING KEPLERATE CLUSTERS IN THE CCVD PROCESS

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Silicon solar cells, produced in industry at large-scale, are based on the p-n junction. The main problem with the creation of such elements is a difficulty in the formation of thin Si layers and the electrical current supply. To solve this problem, in recent years it was propose to combine a semiconductor material, such as silicon, with electrically conductive carbon nanotubes (CNTs). Conductive properties of CNTs depend on their structure, and in the case of multiwalled CNTs the most important parameters are the diameter and defects of the outer nanotube layer. Particularly, defects occurred in the CNT walls provides the p-type conductivity. The structural characteristics can be varied choosing the appropriate method of CNT synthesis.

In this contribution, the formation of hybrid structures from Si and multiwall CNTs was carried out using an aerosol-assistant catalytic chemical vapour deposition (CCVD) method. The iron polyoxomolybdate clusters $[H_4Mo_{72}Fe_{30}O_{254}(CH_3COO)_{10}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8\ (H_2O)\}_3(H_2O)_{87}]\cdot 80H_2O$, so-called keplerates, were taken as catalyst source. The size of the metallic cage is about 2.5 nm, which gives a high chance to obtain thin-wall CNTs. The acetonitrile or alcohol/acetone mixture was used as source for CNT growth. Solution of keplerate (0.1 wt%) in hydrocarbon was injected into tubular CCVD reactor, where the Si substrates of size of 10×10 mm$^2$ were previously located. The synthesis was carried out at temperatures of 800, 900, and 1050°C for 30 min. As a result, the Si substrate was covered by a very thin CNT layer (Fig. 1).

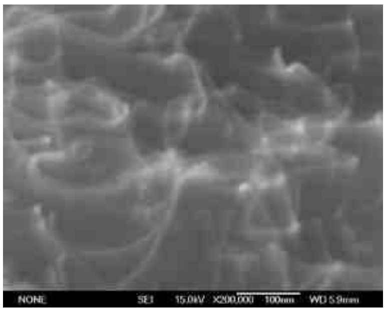

Fig. 1. CNTs grown of Si substrate

The CNT/Si hybrids were tested as solar cell elements. A part of Si substrae was coating with indium titanium oxide (ITO) layer and the sample was placed at a distance of 5 cm from the lamp OI-24. The open circuit voltage, short circuit current, and resistance of the sample under illumination and without that was measured. The most promising results were obtained with the use of CNTs synthesized from an ethanol/acetone mixture at 1050°C. The Raman spectroscopy showed that these CNTs are the most defective and hence they are highly hole-doped.

This work was supported by the Russian Foundation for Basic Research, grant 12-03-00579.

# LASER-INDUCED MODIFICATION OF CARBON NANOTUBES SUSPENSIONS

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The study of laser radiation interaction with nanocarbon materials suspensions is of practical interest for the development of optical power limiters, laser pulse duration control devices, light modulators, modification of nanocarbon materials magnetic properties and etc. We have shown [1, 2] that the onion-like carbon (OLC) suspensions in dimethylformamide (DMF) bleach under the laser radiation pulses of nanosecond duration, to form a new material fraction with pronounced diamagnetic properties. The results obtained were attributed to the chemical reactions between OLC and DMF which resulted in the OLC graphene shells hydration with the formation of non-conducting fragments corresponding to condensed aromatic compounds. To spread this approach on other nanocarbons the experiments of the transformation of multilayer carbon nanotubes (MWNT) suspension in DMF under the high-power laser radiation effect were carried out.

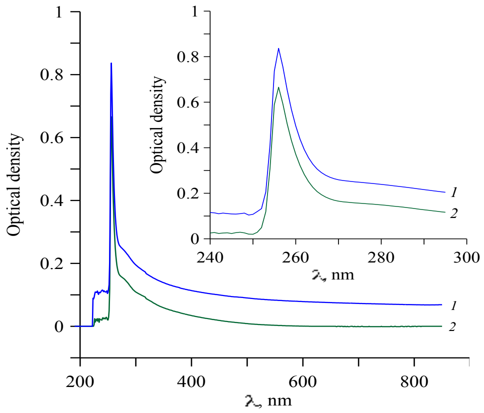

Fig. 1. The optical density of the MCNT suspension layer with respect to pure DMF: 1 – before laser treatment, 2 – after laser treatment

The MWNT were produced by the CVD technology in the reaction of ethylene thermal decomposition. Its average diameter and length were 7-9 nm and 10-20 μm, respectively. The stable suspension of tubes in DMF was obtained using ultrasonic dispersion (22 kHz, 300 W). The MCNT concentration was 0.015 g/l. The suspension was injected into an optical cuvette and affected by the laser pulses, with the duration of 17 ns and the wavelength of 532 nm. It was established that the observable suspension placed in the area of laser beam effect bleaches irreversibly under the laser radiation power density of more than 50 MW/cm$^2$. In the Fig. 1 the optical density of the suspension layer with the thickness of 1.01 mm with respect to pure DMF before and after laser treatment is shown. The CNT suspension in DMF can be seen to bleach irreversibly after the laser treatment over the whole range of the observable wavelengths from 240 to 900 nm. Simultaneously with the bleach effect acquisition the suspension loses its features of the optical power limiting and nonlinear light scattering. This approach can be used for MCNT functionalization by different groups by means of carrying out the reactions with different H-donor compounds under the laser radiation effect. The results are discussed in terms of photoinduced electron transfer (PET) which plays an important role in one-electron reduction [3].

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# MULTI-WALL CARBON NANOSTRUCTURES CHARACTERIZED BY METHOD OF RAMAN SPECTROSCOPY

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Multi-wall carbon nanostructures are very interesting for researchers due to their unique properties, which can be used for a lot application. Thus, for instance, multi-wall carbon nanotubes can be used to create the composite materials with improved properties (polymers, metals, ceramics), the components of electrochemical devices (lithium batteries, supercapacitors), optical elements. For investigation of various forms of carbon nanostructures a Raman spectroscopy technique has been successfully used.

In this work a possibility of the Raman spectroscopy for diagnostics of multiwalled carbon nanotubes and carbon onions has been analyzed. A thermal threshold for ordering of multi-layer structures has been estimated. We investigated several series of samples. Each series consisted of the original material and the material subjected to heat treatment at different temperatures. In the Raman spectra we revealed the changes corresponding to the structure and characteristics modifications of materials. The basic attention has been paid to D (disorder-induced), G (graphite) and 2D (two-phonon scattering)-bands in the Raman spectra.

*This research was partially supported by the RAS research programs, RFBR 12-02-90706-mob_st and FP7 IRSES-247007 project .*

# FINITE-SIZE EFFECTS IN MULTIWALL CARBON NANOTUBE BASED COMPOSITE MATERIAL

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The propagation of azimuthally symmetric guided waves in multiwalled carbon nanotubes (MWCNTs) was analyzed theoretically in the terahertz and sub-terahertz regimes. We modeled the shells of an MWCNT as impedance sheets with axially directed surface conductivity [1], ignored intershell tunneling of electrons but incorporated electromagnetic intershell coupling, in an integral-equation approach [2].

The electromagnetic responses of MWCNTs of different cross-sectional radius (3-30 nm) and finite length were theoretically studied in the terahertz and sub-terahertz regimes. The finite length leads to the appearance of a terahertz peak in the MWNT polarizability spectrum, the frequency of the peak depending on the length and the number of metallic shells. Semiconducting shells of small radius in an MWNT do not significantly affect the polarizability. At lower frequencies, a strong depolarizing field creates a shielding effect [3]: the penetration depth of the axial component of incident field depends on the frequency, the length, and the electron relaxation time. This strong screening effect can be exploited in MWNT-interconnects, whose inner metallic shells are used to propagate signals while being shielded from spurious radiation by the outer metallic shells.

The effective parameters of MWCNTs based composite material were calculated on the basis of Maxwell Garnett approach. The dependence of the effective permittivity on nanotube diameter and length was demonstrated. It was established, that thinner MWCNTs are preferable for creation composite material with higher conductivity, whereas thicker MWCNTs are preferable for creation composite material with higher real part of permittivity. Thus, the analysis carried out in this work forms a basis for the design and development of composite material containing MWCNTs as inclusions.

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# ELECTRONIC STRUCTURE OF CYLINDRICAL GASE QUANTUM DOTS

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Semiconductor quantum dots are of particular interest for electronic and optoelectronic applications. Beside the well known spherical quantum dots, nanocrystals of layered semiconductors like GaSe or InSe with cylindrical shape have been successfully synthesized and characterized [1]. These nanoobjects exhibit high quantum yields, high photostability and strong structural anisotropy. In opposite to spherical quantum dots with passivated surfaces, cylindrical quantum dots can strongly couple to each other [2,3]. These properties make such quantum dots an attractive material for optoelectronic and charge transfer devices.

In the present work, the electronic structure of cylindrical GaSe quantum dots was investigated within the empirical pseudopotential method with use of the truncated crystal approach. This method is known to give more accurate results than the simple effective mass approximation. The dependence of the HOMO-LUMO gaps on the radius of the cylindrical quantum dots is presented.

*This work was supported by RFBR-12-07-90700-mob_st project, by the Russian President Grants (MK-1777.2012.2 and MK-5618.2012.2) and by FP7 IRSES 247007 project.*

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# *AB INITIO* STUDY OF IODINE-DOPED SINGLE-WALLED CARBON NANOTUBES

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In this work we have investigated a structural stability and electronic properties of single-walled carbon nanotubes (CNTs) as matrices for various iodine configurations inside.

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

We have used an ultrasoft pseudopotential [2] for the carbon atoms and a planewave cutoff of 450 eV. The optimal atomic positions were determined by a convergence of a total energy with an accuracy of 0.3 meV. We have adopted a supercell model in which the CNTs considered were arranged with their adjacent outer walls separated by 10 nm.

The binding energies were calculated as the difference in total energy between the compound and a pseudoatomic calculation done for the same cutoff [3]. A linear configuration with $I_2$ bond length equal to 2.84Å has been found as the most stable, that well correlated with the experimental data[4].

The obtained results for the band structures have shown that all considered semiconductor nanotubes have changed the type of conductivity to metallic. It can be explained by the charge transfer between CNTs and iodine dopands inside.

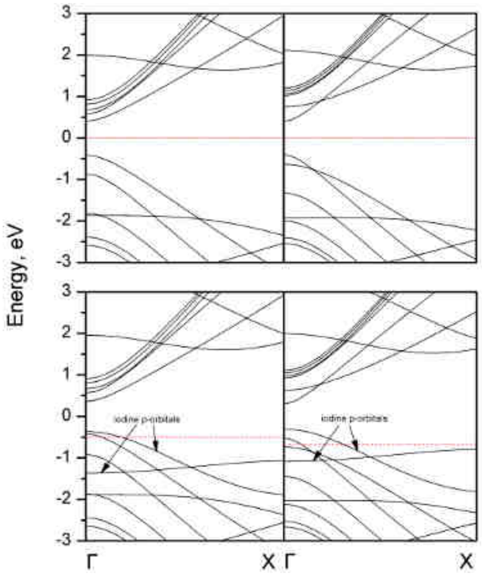

Fig. 1. Band structures of pure (top) and iodine-doped (bottom) carbon nanotubes.

*This work was supported by RFBR-12-07-90700-mob-st project, by the Russian President Grant (MK-1777.2012.2) and by RAS research programs.*

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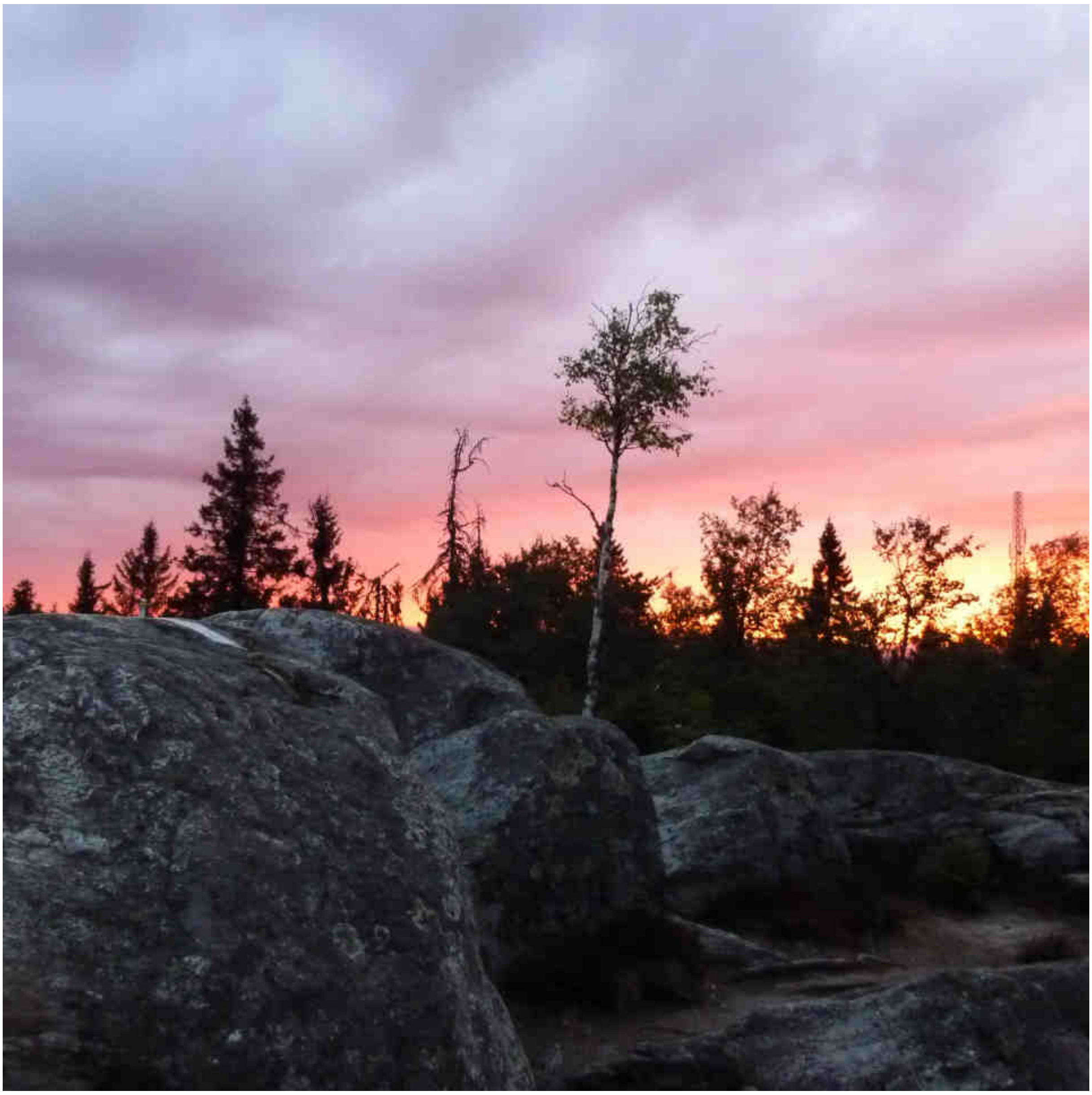

# OPTICAL MATERIALS AND NANOMATERIALS FOR NONLINEAR OPTI APPLICATIONS

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## Technical Abstract

This presentation will focus on the use of optical and nanomaterials for nonlinear optical applications. Two examples will be discussed, (1) the use of nanocarbone and Carbone nanotubes as saturable absorbers in short pulse fiber lasers, and (2) the use of nanomaterials such as $C_{60}$ as well as gold nanoparticles as sensitizers in photorefractive (PR) polymer for updateable 3D holographic display. As part of example 1, a new platform for investigation of nonlinear liquids in liquid core optical fibers (LCOF) will be described and its applications in generation of new frequencies by Raman processes in $CS_2$-filled LCOF will be covered [1]. In the second example, large area PR polymer 3D displays for telepresence application will be summarized [2].

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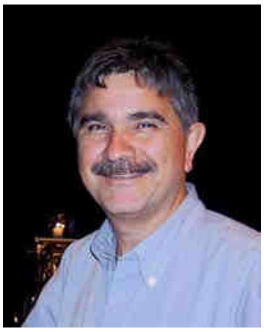
## Biography



Nasser Peyghambarian is a Professor at the College of Optical Sciences and also at the Department of Materials Science & Engineering at the University of Arizona. He is the Chair of Photonics and Lasers and serves as Director of the NSF Center for Integrated Access Networks (CIAN). He is Chairman of the Board and Founder of NP Photonics, Inc and TIPD, LLC. He received his Ph.D. in solid-state physics from Indiana University in 1982, specializing in optical properties of semiconductors before joining the optics program at the University of Arizona. He is the recipient of the International Francqui Chair, Belgium 1998-1999. He is a Fellow of the Optical Society of America, the American Physical Society, Society of optical engineers, SPIE and the American Association for the Advancement of Science.

# FROM CARRIER MULTIPLICATION AND HOT-ELECTRON TRANSFER TO THE MYSTERIES OF NANOCRYSTAL BLINKING

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Due to “sub-excitonic” dimensions, nanocrystal quantum dots can produce novel electronic interactions that involve charges residing in intrinsic quantized states as well as species located at nanocrystal surfaces. For example, the interaction of a hot conduction-band electron with valence-band charges can lead to an interesting relaxation regime in which the kinetic energy of a hot carrier is not lost as heat but is used to produce additional electron-hole pairs, a process known as carrier multiplication [1]. Our recent work in this area includes the development of reliable methods for efficient screening of carrier multiplication performance of infra-red emitting nanocrystal quantum dots using photon counting with superconducting nanowire detectors, the studies of the impact of “extraneous” processes on quantitative measurements of this process [2], and the evaluation of the effects of the nanocrystal composition, dimensions, and shape on multiexciton yields. An interesting “byproduct” of these studies has been the observation of high-efficiency hot-carrier transfer that has a significant effect on quantitative measurement of carrier multiplication yields [3]. Surprisingly, we also observe that escape of hot electrons from the nanocrystals has direct relevance to another puzzle in the nanocrystal field – nanocrystal blinking [4]. By conducting measurements of fluorescence intermittency in individual quantum dots, while controlling the degree of their charging via electrochemical means, we detect two distinct blinking regimes. The first is consistent with the traditional concept of charging and discharging of the quantum dot core. In this model a charged state is “dark” due to highly efficient nonradiative Auger recombination. The second mechanism, however, is somewhat a surprise; the majority of the quantum dots display blinking due to the filling and emptying of a trap on the surface of the dot. If not occupied, this trap intercepts a hot electron prior to its relaxation into the emitting state, thus causing a “blink.” Importantly blinking can be controlled and even completely suppressed electrochemically by applying an appropriate potential. Finally, I will overview our work on the development of a new generation of quantum dots that in addition to stable blinking-free emission show a significant suppression of nonradiative of Auger recombination [5]. Such dots are promising candidates for applications in future solution processable devices from lasers and light emitting diodes to sources of single photons.

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Recent developments in ultra-short pulsed laser technologies have enabled ultrafast optical manipulation of low-energy excitations in solids, for example, phonons and magnons. In particular, Raman-induced nonlinear optical processes offer an attractive opportunity of ultra-fast control without heating. In coherent scattering on the low-energy excitations, the conservation laws of energy, momentum and angular momentum determine the frequency, wave vector, and polarization of the scattered photons, respectively [1]. In particular, the latter implies that angular momentum of the electromagnetic field ($\boldsymbol{J}^{EM}$), collective excitations ($\boldsymbol{J}^{ex}$), and the crystalline lattice ($\boldsymbol{J}^{c}$) satisfy the following relationship: $\boldsymbol{J}^{EM}+\boldsymbol{J}^{ex}+\boldsymbol{J}^{c}=0$. When light propagates in the medium along a continuous rotational axis Z, $J_z^{\mathrm{c}}$ is a conserved quantity and thus $J_z^{\mathrm{EM}}+J_z^{\mathrm{ex}}$ is also conserved. In contrast, when light propagates along a threefold rotational axis, the crystal quasi angular momentum is conserved and thus $J_z^{\mathrm{EM}}+J_z^{\mathrm{ex}}$ can be changed in the process of the light scattering by $3N\hbar$, where $N$ is an integer. Such an analogue of the Umklapp process [1] is known for decades in nonlinear optics. It determines in particular the polarization selection rules in the second-harmonic generation[2] and parametric down-conversion [3]. However, until now a little attention has been paid to implications of the discrete rotational symmetry for the coherent control of low-energy excitations.

We have recently demonstrated that the angular momentum conservation enables optical manipulation of magnetization vector in multi-domain antiferromagnetic NiO. The [111] axis of this crystal is effectively threefold because all the domains contribute to the optical process coherently. We observed magnetic dipole terahertz radiation, which originates from the magnetization oscillations induced by linearly polarized femtosecond laser pulses. The relationship between the polarization azimuths of the incident light beam and generated terahertz wave can be excellently interpreted in terms of the angular momentum conservation [4]. In addition, we achieved control of magnetic oscillations by employing polarization-twisted double pulse excitation [5]. The angular momentum conservation manifests itself also in terahertz radiation via optical rectification in a ZnTe single crystal when the excitation beam propagates along its threefold [111] axis. By the vectorial pulse shaping, we select *envelope helicity* [6] of the excitation femtosecond pulse and control the helicity of the terahertz radiation.

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# ORGANIC OPTO NEURONAL INTERFACES FOR ARTIFICIAL RETINA AND LIFE ENHANCING TECHNOLOGY

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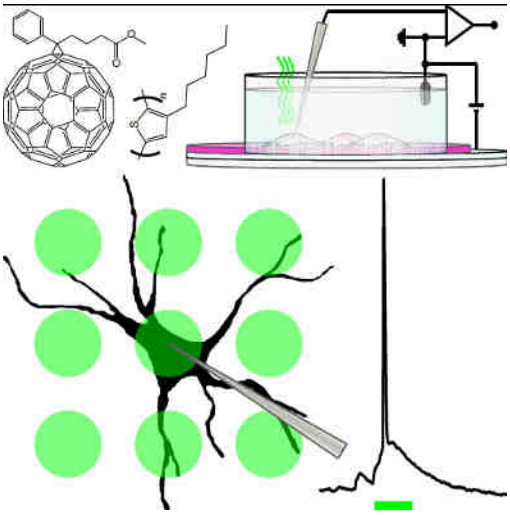
A key issue in the realization of retinal prosthetic devices is reliable transduction of the information carried by light into specific patterns of electrical activity in the networks involved in visual information processing. Soft organic materials can be used to couple artificial sensors with neuronal tissues. Here, we interface a network of primary neurons with an organic blend. We show that primary neurons can be successfully grown onto the polymer layer, without affecting the optoelectronic properties of the active material or the biological functionality of the neuronal network. Moreover, action potentials can be triggered in a temporally reliable and spatially selective manner with short pulses of visible light. Our results may lead to new neuronal communication and photo-manipulation techniques, thus paving the way to the development of artificial retinas and other neuro-prosthetic interfaces based on organic photo-detectors.



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# Thursday, August 2

# CARBON-NANOTUBE-BASED PLASTIC ELECTRONICS

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Flexible devices will change the style of electronics products such as mobile phone and e-papers [1]. Carbon nanotube (CNT) thin films are expected to realize such devices with high performance by simple and low-cost fabrication processes. In the presentation, I will talk about our recent progresses of flexible thin-film transistors (TFTs) and integrated circuits (ICs) based on CNT thin film.

First, we developed the gas-phase filtration and transfer process to form carbon nanotube thin film with high-carrier mobility [2]. The CNTs were continuously grown by atmospheric-pressure floating-catalyst CVD technique [3]. The nanotubes were then collected on a membrane filter for a few seconds at room temperature and atmospheric pressure, and then transferred onto the substrate. The carbon nanotube TFT fabricated on a Si substrate, showing excellent performance with a mobility of >600 $cm^2/Vs$ and on/off ratio of $>10^6$. The high mobility can be attributed to the clean and long nanotubes and unique morphology of the nanotube networks formed by 'Y'-shaped junctions.

ICs, including basic logics (NOT, NAND, NOR), ring oscillators, flip-flops (RS-FF and D-FF), were fabricated on a transparent and flexible plastic substrate. Robust and repeatable operations were obtained for these ICs. The master-slave D-FFs, that consist of 8 NANDs and 2 NOTs, showed the edge-triggered latching behavior. A 21-stage ring oscillator in which 44 TFTs were integrated showed a delay time of 12 μs per stage for a channel length of 100 μm.

We also report all-carbon TFTs and ICs, in which all materials are organics or carbon materials. The active channels and passive elements (electrodes, interconnections) have been formed by CNT thin film. The devices were fabricated on a PEN film substrate. Thick CNT films (transparency: 85 % at 550 nm, sheet resistance: 150 Ω/sq) were used for passive elements. A 660-nm-thick PMMA was used as the gate insulator. The all-carbon TFT showed on/off ratio of $\sim 10^5$ and mobility of 1,027 $cm^2/Vs$. Various kinds of functional integrated circuits were operated at a relatively low voltage of 5 V. A bending test verified the good flexibility of the all-carbon devices.

We fabricated CNT TFTs by flexo printing technique which is a high-throughput, typographic press with a photopolymer stamp. The contact electrodes were formed by printing Ag-nanoparticle ink by a flexo printer. The throughput of our prototype flexo printer was 6.6 cm/s. The device showed a mobility of 51.5 $cm^2/Vs$.

Acknowledgments: This work is partially supported by Industrial Technology Research Grant Program in '08 from NEDO, ALCA and A-STEP by JST, R&D promotion scheme funding international joint research promoted by NICT, Aalto Univ. MIDE program.

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# GRAPHENE BASED MATERIALS FOR NON-LINEAR OPTICAL APPLICATIONS AND ULTRAFAST LASER APPLICATIONS

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In very recent years, graphene has become the focus of significant research efforts. Characteristics such as potential near-ballistic transport and high mobility make graphene viable as a material for nanoelectronics. Not only this, but its mechanical, electronic and thermal properties are also perfect for mirco- and nanoscale mechanical systems, thin film transistors, and transparent and conductive composites and electrodes. In this work, particular interest was afforded to the 2μm wavelength and to the modelocking capabilities of graphene, exploiting its optoelectronic properties to achieve this. Graphene is a prime candidate for several reasons, including its intrinsic broadband operation capabilities due to the gapless linear dispersion of Dirac electrons. Non-linear saturable absorption is required for materials used as a mode locker in lasers to obtain light pulses of very short duration, in the order of femtoseconds.

Fig.1. Graphene/THF dispersions

High yields of graphene were prepared via liquid-phase exfoliation of powdered graphite. This was achieved through the use of methods devised by J. N. Coleman et al.[1] and other groups[2]. These methods rely on the exfoliation and stabilization of graphene using special solvents or surfactants, combined with long sonication times (~170 hours). Unfortunately, commonly used solvents, such as water, have strong absorption peaks at 2μm. Therefore, initially, potential solvents were tested for their suitability, both for transparency at 2μm and for dispersions of graphene. A promising solvent, tetrahydrofuran (THF), was the first to be tested (figure 1), primarily due to its almost complete transparency at 2μm and its ability to dissolve important polymers, such as Poly(methyl methacrylate) (PMMA). Dispersions of graphene with N-Methyl-2-pyrrolidone (NMP) as the solvent were also produced. While it does have slight absorption at 2μm, it is proven to both provide efficient dispersions of graphene, and to dissolve polymers such as PMMA. Afterwhich, the dispersions as well as thin films were examined using various apparatus, including UV-Vis-IR spectrometer, raman spectroscopy and z-scan techniques.

Nonlinear optical properties are routinely examined using the so-called z-scan method. This set up consists of a thin sample being moved through the focus of a laser beam to vary the light intensity on the sample. This allows for measurement of the non-linear index $n_2$ Kerr nonlinearity with the “closed” aperture method, and the non-linear absorption coefficient $\Delta\alpha$ via the “open” aperture method.

Funding from the ISLA project, which aims to develop a set of “building block” components for 2μm lasers, is gratefully acknowledged.

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# RADIO-FREQUENCY CAVITY READOUT OF STAMP TRANSFERRED GRAPHENE MECHANICAL RESONATORS

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We present a study on graphene mechanical resonators with radio-frequency (RF) cavities. A novel stamp technique was developed to transfer suspended graphene flakes onto any substrate and to assemble them with small localized gates into mechanical resonators. The mechanical motion of grapheme is detected using an electrical RF cavity readout where the time-varying graphene capacitor modulates a RF carrier at $f =$ 5-6 GHz producing sidebands at $f \pm f_m$. A mechanical resonance frequency up to $f_m =$ 178 MHz is demonstrated. We find both hardening/softening Duffing effects on different samples and obtain a critical amplitude of ~ 40 pm for the onset of nonlinearity in graphene mechanical resonators. Measurements of the quality factor of the mechanical resonance as a function of DC bias voltage $V_{dc}$ indicates that dissipation due to motion-induced displacement currents in graphene electrode is important at high frequencies and large $V_{dc}$ [1]. Besides the normal metal, low-Q LC tank, superconducting circuits are developed as high-Q RF cavities to improve the detection sensitivity, aiming at the thermal motion and quantum limit of the graphene mechanical resonators.

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# Detonation Nanodiamond Particles in Electronic and Optical Applications

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Recent achievements in production of colloidal suspensions of individual nanodiamond particles only 4-5nm in size (so called single-digit nanodiamond) and the controlled production of nitrogen-vacancy centers in nanoscale diamond opened unprecedented perspectives in electronics and optical applications of nanodiamonds. Production of nanodiamond particles containing specific impurity defects seems poised to revolutionize biological imaging and quantum optics applications, while nanometer-sized diamond particles are indispensable for seeding of substrates for growth of diamond films by chemical vapor deposition. The range of applications of NDs in electronics can be very broad if electrically conductive ND particles can be synthesized. Production of conductive doped ND particles can be very beneficial in high surface area carbon electrodes for electroanalysis, electrochemical double-layer capacitors, storage materials for batteries and other applications. Nanodiamond-derived conductive onion-like carbon nanoparticles are already being explored in carbon electrodes applications.

The two major breakthroughs, the production of ND particles 4-5nm in size and ND particles containing impurity defects exhibiting stable luminescence and unique spin properties are related to nanodiamond particles synthesized by different techniques, detonation of explosives and grinding of HPHT diamond, correspondingly. Owing to the lack of optically active particles containing NV centers in useful amounts, ND synthesized from explosives is generally not amongst the preferred candidates for imaging applications. In this paper, systematic studies on nitrogen control in NDs produced by detonation shock wave-assisted synthesis will be reported. Nitrogen content in representative classes of NDs produced by detonation shock wave conversion of different carbon precursor materials, namely graphite and a graphite\hexogen mixture into ND, as well as ND produced from different combinations of explosives using different cooling methods (wet or dry cooling) will be discussed. Perspectives of production of NV centers in detonation NDs (DND) will be summarized. Perspectives in the production of photoluminescent DNDs imparted by other means will be also discussed. Namely, it will be reported that carbon dots decorated DND can be produced from detonation soot demonstrating surprisingly strong photoluminescence of different colors depending on the conditions of treatment and the type of soot treated. Other recent advances in DND applications, particularly in seeding of substrates will be briefly surveyed and areas of future scientific research highlighted.

# FABRICATION OF CARBON NANOSTRUCTURES BY LASER AND SPM ABLATION TECHNIQUES

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It will be shown that laser is an effective tool for surface nanostructuring of diamond materials: single crystal, poly and nanocrystalline diamond, diamond-like coatings [1]. The key element in laser nanoprocessing of these materials is phase transformation "diamond-graphite". In the case of thermal surface graphitization, which takes place at $T \geq T_g \approx 700^0C$ ($T_g$ – graphitization threshold), conducting nanofeatures with lateral resolution as low as $\lambda/2$ ($\lambda$ - laser wavelength) and thickness ranging from 10 nm up to 100 nm were fabricated. There are two major routes how to remove (ablate) laser graphitized material: vaporization ($T \geq T_V \approx 4000^0C$) and reactive chemical etching, e.g. oxidation. It is found that for short laser pulses and $T_g < T < T_v$ etching rates can be as low as $10^{-1}$-$10^{-3}$ nm/pulse – this regime was called reactive nanoablation and allows to obtain ultra-fine diamond structures. Moreover, in the case of clear diamond crystals nanoablation with even smaller rates $10^{-3}$-$10^{-4}$ nm/pulse can be performed at $T < T_g$ as a result of formation and oxidation of weekly bounded carbon atoms and clusters.

Another technique [2] of carbon ablative nanostructuring can be used for conductive carbon materials, such as graphite and graphene. Instead of a laser beam, electrical pulses should be applied to the sharp conductive (silicon) cantilever of a scanning probe mocroscope (SPM). To remove (ablate) carbon material from the area between the needle tip and graphene sheet, the positive electrical pulse polarity and sufficient pressure of the probe should be combined. The first condition leads to delivery of hydroxyl and oxygen ions from the adsorbed water to the substrate surface and formation of less dense thin layer (clusters) of graphite oxide and soot. This material is removed mechanically by the scanning probe. Nanostructures on the surface of highly oriented graphite with spacial resolution of about 10-15 nm (close to the used cantilever tip radius) have been demonstrated. Advantage of application of bipolar electrical pulses will be discussed.

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# INVESTIGATION OF CVD DIAMOND BY THERMAL OXIDATION

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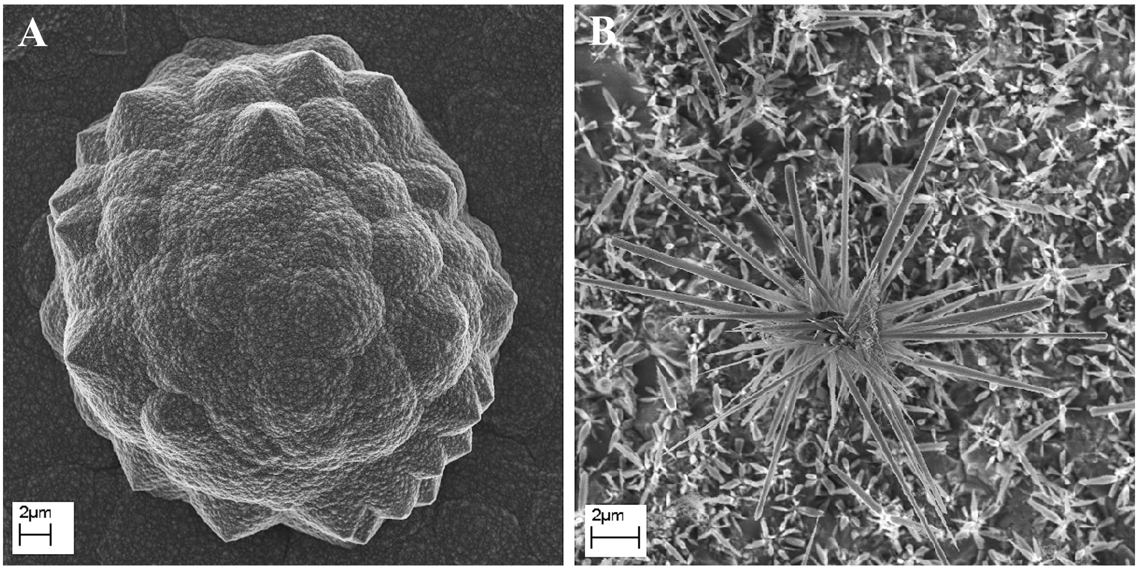
Diamond films were obtained by a direct current plasma enchanced chemical vapor deposition (DC PECVD) with different methane concentrations. Correlation of the CVD process parameters with a structure and composition of the films via using Raman spectroscopy and scanning electron microscopy (SEM) was investigated.

A thermal oxidation process of the diamond films has been comprehensively studied. The oxidation was realized via heating of the CVD films in $O_2$ atmosphere with a temperature allowing etching of the smallest fraction of the diamond crystallites in the films. Pristine and oxidized CVD diamond films were analyzed with Raman spectroscopy and SEM techniques. Raman spectroscopy revealed substantial changes in the polycrystalline diamond film composition induced by oxidation [1]. A selective oxidation of disordered carbon and smallest size diamond crystallites was obtained at appropriate temperatures. A model explaining the formation and oxidation of the CVD diamond films containing the micrometer single diamond cores surrounded by the nanocrystalline diamond and disordered carbon has been proposed on the basis of the obtained results.



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

[1] Aleksey A. Zolotukhin, Rinat R. Ismagilov, Matvei A. Dolganov, and Alexander N. Obraztsov; Journal of Nanoelectronics and Optoelectronics, Vol. 7, No 1. (2012), 22-28.

# SIGMASCAN SCANNING PROBE MICROSCOPES

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In talk, the main products of Sigma Scan Ltd. in a field of ultra high vacuum scanning probe microscopy (SPM) will be presented and discussed. Besides, set of SPM applications for atomic scale research in a field of chemical surface reactions will be presented too. Taking into account new ability of SPM in engineering processes [1], the ideas how to create new atomic scale technological procedures under ultra high and extremely high vacuum will be discussed.

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# MICROWAVE PROBING AND ELECTRICAL PROPERTIES OF PYROLITIC CARBON THIN FILMS

P. Kuzhir[1], A. Paddubskaya[1], K. Batrakov[1], S. Maksimenko[1], V. Ksenevich[2], T. Kaplas[3] and Yu. Svirko[3]

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We report on the first experimental study of the electromagnetic (EM) absorption properties of pyrolitic carbon thin films produced at quartz substrate via CVD method at 1100 $^{o}$C at CH4:H2 gas atmosphere in low pressure (20 mBar). Thickness of the film is controlled by the CH4:H2 ratio and found to be between 5 and 40 nm. The films exhibits high conductivity (sheet resistance was found to be in the range of ~150~700 Ohm) and low negative temperature coefficient of resistance (R(2K)/R(300K)<2) indicating thus on dominating role of $sp^2$-hybridization in their electrical properties. The EM attenuation in Ka-band (26-37 GHz) was found to be very dependent on the thickness of the film and relatively high: only 40% of microwave signal pass through the sample when the thickness is 40 nm (see Fig.1). The EM shielding effectiveness of pyrolitic carbon is caused mostly by the absorption of microwave signal, which rises monotonously from 5% to 35% when the thickness of thin films increase from 5 to 40 nm. The physical reasons for such an unexpectedly high absorption provided by thin films which are thousands times thinner than skin depth in microwave range are also discussed. To conclude, pyrolitic carbon thin films could be a promising tool for microwave application as specific frequency bands filters.

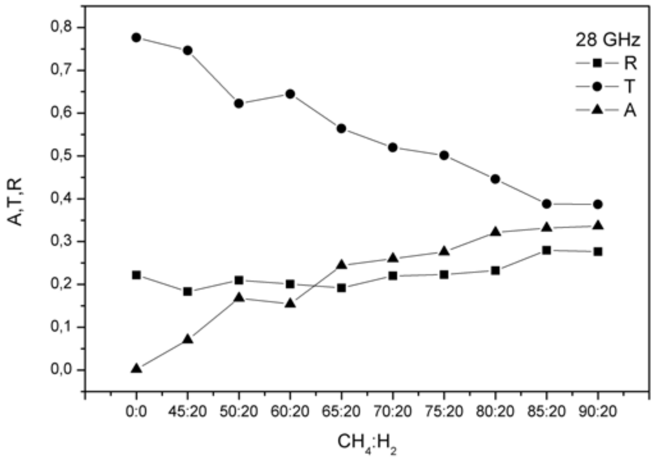

Fig.1. The dependence of absorption/ reflection/ transmission of pyrolitic carbon thin films on film thickness in microwave range.

# PYROLYTIC CARBON COATING OF OPTICAL SUB-MICRON STRUCTURES

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Polycrystalline graphite made by gaseous pyrolysis is well known form of $sp^2$ bonded carbon. This material is often referred to as pyrolytic carbon (PyC) and has been studied for more than 50 years. Until very recently this material was manufactured in the bulk form and has not been very interesting in optical point of view. However, recent advances in chemical vapour deposition (CVD) have opened novel methods to produce ultrathin, semitransparent, conducting PyC films directly on arbitrary substrates [1]. We demonstrate here that nanometrically thin PyC films can be synthesized on the surface of dielectric nanogratings, which can be employed e.g. for electro-optical applications or surface area expansion.

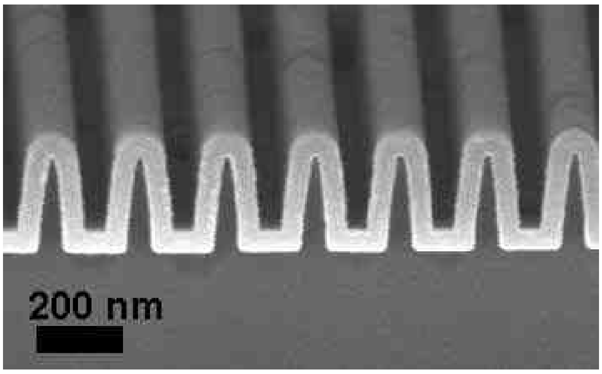

Fig. 1 Scanning electron microscope picture of PyC coated nanograting on quartz substrate.

In our experiments we prepared optical gratings on three different substrates including quartz, silicon and e-beam evaporated TiO2 on quartz. These substrates were patterned by e-beam lithography with different sized gratings starting from 200 nm periods and a thin PyC film was synthesized over the grating by methane based CVD. Although the film deposition took place at temperature of about 1100 °C necessary for decomposition of the methane, silicon and quartz gratings remains intact. We observed some minor structural changes in evaporated $TiO_2$ layer which, however, did not affect to the grating properties.

In conclusion we have demonstrated semitransparent PyC deposition on top of optical nanogratings. The homogeneity and uniformity of the film is very high and thus the quality of the conductive carbon coating is sufficient to various optical applications.

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# UNIFORM COATING FORMATION BY CHEMICAL VAPOR DEPOSITION

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We present results of investigations directed on revealing of effect of the key process parameters on uniformity of coatings obtained by a chemical vapor deposition (CVD) techniques exploring a plasma enhancement with DC-discharge, plasma jet, and hot filament activation methods. The coating materials were crystalline nanostructures, including diamond- and graphite-like nanocarbons [1-3]. In particular, the shapes (regular tetragon, rectangle, and circle) of silicon substrates, the configurations of the electrodes (for DC PECVD), nozzles (for plasma jet CVD), filaments (for HF CVD) were simulated to find the most appropriate conditions for obtaining the uniform coatings.

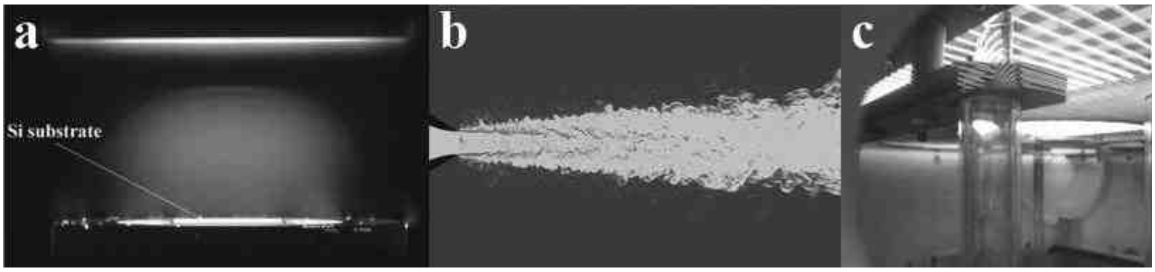

*Fig. 1. Several types of CVD: (a) photo of plasma ball in DC-discharge CVD, (b) model of activated region in Plasma Jet, (c) reactor image during Hot Filament CVD*

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# ANISOTROPIC ELECTROMAGNETIC RESPONSE OF CARBON NANOTUBE IN TERAHERTZ AND GIGAHERTZ FREQUENCY RANGE

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Mechanism of high-frequency radiation scattering by multiwall carbon nanotubes (MWCNTs) with metallic conductivity differs from the classical model as proposed theoretically. One can expect that nanotubes distributed homogenously in polymer dielectric matrix would exhibit properties of tiny directional antennas capable to resonantly propagate the electromagnetic waves. Recently we have found that stretched polymer filled by MWCNTs exhibits anisotropic absorption in the gigahertz region (26-37 GHz) [1] and that produced by the forge-rolling method samples contained MWCNT strongly anisotropic in terahertz region (1-10 THz) [2]. The THz and GHz measurements have different sensitivity in relation to the MWNT concentration in a sample. In the samples examined in terahertz region the quantity of MWNT in polymeric matrix was less percolation threshold.

Anisotropic composite materials have been prepared by repeated forge rolling of polystyrene contained carbon nanotubes (CNTs) with a length of 63 μm. The THz transmission and reflection spectra of the composites were recorded on a vacuum Fourier spectrometer IFS-66vs for two polarizations of electric field vector. Transmission contrast characterizing the polarization asymmetry reached 20 in the central part of sample. Reflection signal for parallel polarization was twice higher than the signal for perpendicular polarization. Anisotropic response of composites was measured on the Novosibirsk free electrons laser (FEL) at 130-μm length and the angular dependence of transmission was determined (Fig. 1). It was observed that contrast decreases beginning from the wave length ~100 μm that could be explain by different length of CNTs occurred in the sample.

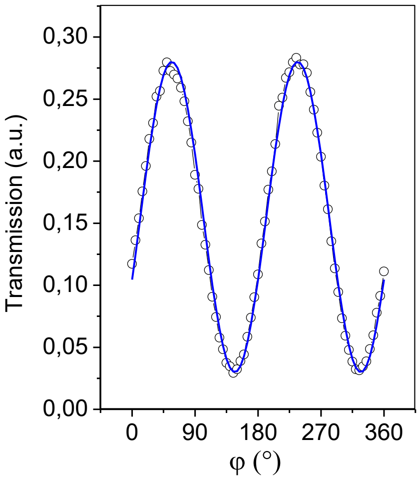

Fig. 1. Anisotropy of terahertz radiation transmission measured on the FEL at λ = 130 μm wave length (dotted line) and approximation of the experimental data by a function $\cos^2(\phi)$ (solid line).

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# ELECTRONIC STRUCTURE OF IDEAL AND DOPED SINGLE-WALL CARBON NANOTUBES CALCULATED USING AUGMENTED CYLINDRICAL WAVE METHOD

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Carbon nanotubes are an important class of nanomaterials. We develop a new quantum-mechanical method for calculating the electronic structure of the chiral nanotubes both perfect and having impurities. This is the linear augmented cylindrical wave (LACW) method. The main argument for using cylindrical waves is to account for the cylindrical geometry of the nanotubes in an explicit form that offers the obvious advantages. In this model, the electronic spectrum of the single-wall nanotubes is governed by movement of electrons in the interatomic space of cylindrical layer and by scattering of electrons on the atomic spheres. Every tubule can be generated by first mapping only two nearest-neighbor C atoms onto a surface of a cylinder and then using the rotational and helical symmetry operators to determine the remainder of the tubule. In the symmetry-adapted version of the method, the cells contain only two carbon atoms, and the theory becomes applicable to any tubule independent of the number of atoms in the translational unit cell. The method is implemented as program package and applied to determine the total band structures and densities of states of the chiral semiconducting and metallic both pure and intercalated single-wall carbon tubules. Based on a Green’s function technique, the first-principles numerical method for calculation of the electronic structure of the point impurities in the chiral tubules is elaborated. The host tubule electron Green’s function is calculated using the LACW theory. The Green’s function of the impurities is calculated in the terms of matrix Dyson equation. A relativistic version of the LACW method is developed and used for calculating the spin-orbit gaps in the armchair tubules.

This work supported by Russian Basic Research Foundation (grant 11-03-00691) and EU FP7 under Project 247007 CACOMEL.

# DEFORMATIONS OF CARBON NANOTUBES

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There are three types of deformations which does not break the symmetry[1] of carbon nanotubes: stretching, breathing and torsion. We use this fact to make efficient symmetry based calculations of the properties of nanotubes during such deformations. Among the considered properties are electronic ones (conductivity, density of states), electro-optical (absorption) and Raman spectra. For a number of tubes, we use full symmetry implemented code POLSym to monitor effects of deformation in the range of several percents, i.e. within linear response regime.

In fact, the symmetry group of the carbon nanotubes is line group, $\boldsymbol{L}_{\mathrm{C}}=\boldsymbol{T}_{Q}(f)\boldsymbol{D}_{n}$ for chiral, and $\boldsymbol{L}_{\mathrm{A}}=\boldsymbol{T}_{2n}(f)\boldsymbol{D}_{n\mathrm{h}}$ for achiral tubes. Here, $\boldsymbol{T}_{Q}(f)$ is helical cyclic group, generated by $(C_Q|f)$, rotation for $2\pi/Q$ followed by translation for $f$ along tube axis, $\boldsymbol{D}_n$ is diedral group generated by rotations $C_n$ for $2\pi/n$ around tube axis and horizontal $U$ axis, while horizontal and vertical mirror planes are additionally present in $\boldsymbol{D}_{n\mathrm{h}}$. Each nanotube is completely determined by its single atom, as the action of the group on this atom gives all other atoms. Therefore, the only independent configuration parameters are coordinates $(D/2,\phi,z)$ of the initial atom, and continual group parameters $Q$ and $f$. Notet hat the change of the former does not change the symmetry, since new symmetry group (of the deformed nanotube) is isomorphic to the initial one. Therefore, nanotube diameter $D$, $Q$ and $f$ are parameters which are varied during our analysis, and they correspond to breathing, torsion and stretching, respectively.

The calculations are performed as follows. The deformation parameter is fixed to the chosen value (in the mentioned range), and then the system is relaxed regarding all other parameters. In this, relaxed deformed configuration various properties of nanotube are looked for. Finally, these properties are analyzed as a function of the deformation parameters, for all three deformations.

Several features are found. The most striking one is pseudo periodic behaviour of gap during the torsion. Also, interesting effects on the phonon didplacements are found, which affect Raman spectra through selection rules.

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# STRAIN ENGINEERING OF CARBON NANOCOILS' ELECTRONIC BAND STRUCTURE AND OPTICAL ABSORPTION SPECTRA

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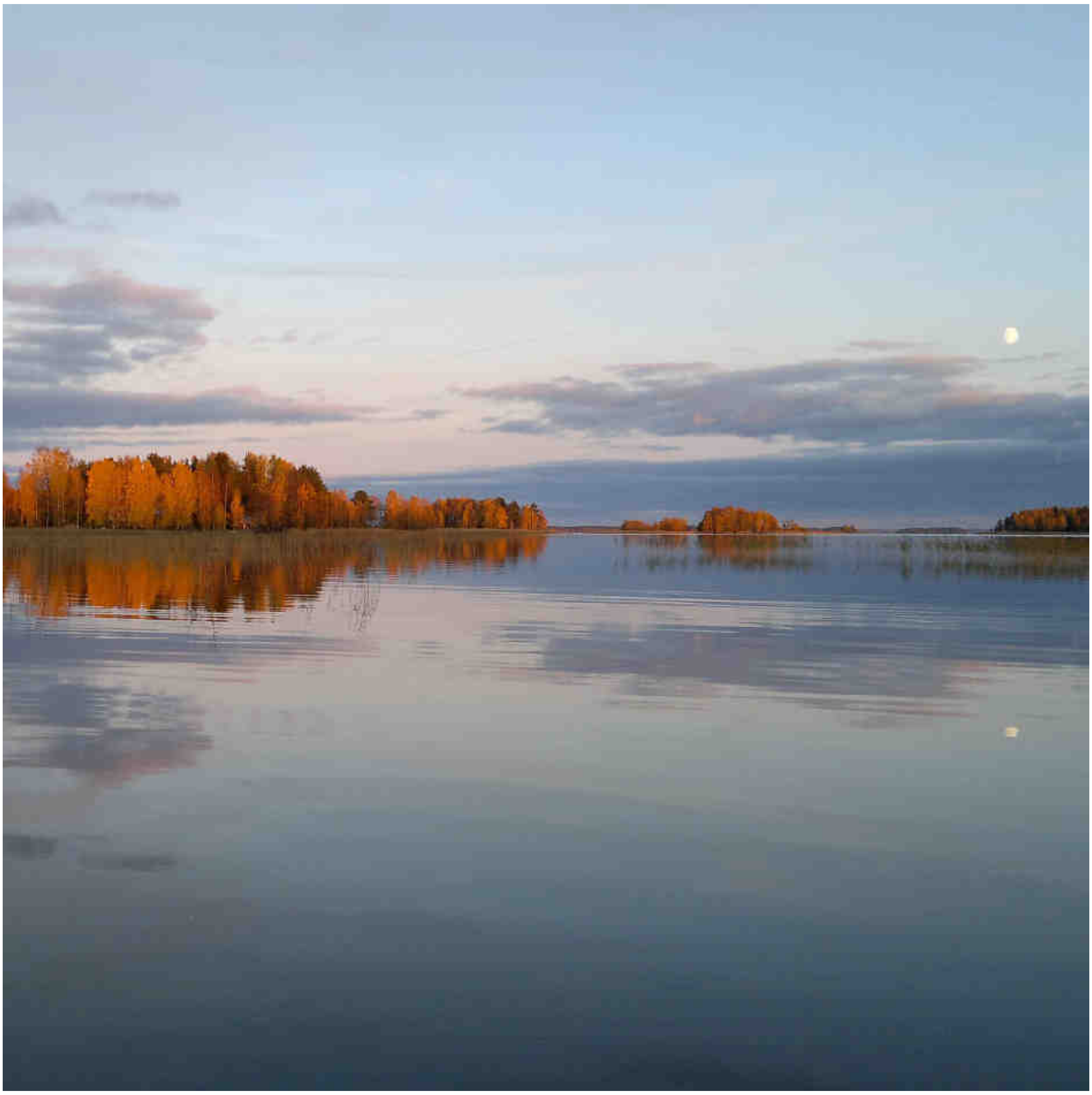
Helically coiled carbon nanotubes (HCCNTs) were predicted in the early 90-ies and a few years later their experimental observation has been reported. Nowadays they are produced at high yield and selectively, by catalytic chemical vapor deposition. CNTs with regular coiled structure can be generated by periodic incorporation of pentagons and heptagons into a hexagonal carbon net. Such a modification of a graphitic network induces significant changes in the electronic band structure and HCCNTs possess electrical and magnetic properties, which are different from that of the straight CNTs.

Due to their unique structure carbon nanocoils (CNCs) exhibit also remarkable mechanical properties showing super-elastic spring-like behavior. Experimentally, HCCNTs have been elastically elongated to a maximum strain of 42%. Our numerical simulations show that elongation of the coils, as large as 250% induces at most 3.5% relative bond length change predicting thus extreme large elasticity of these structures.

Here, theoretical study of the electronic band structure and optical conductivity of the relaxed single-walled HCCNTs is performed. It is shown that according to the electronic band structure CNCs can be categorized as either (in)direct or narrow gap semiconductors (SC) or as semimetals. Also, the effect of uniaxial strain on the electronic band structure and optical absorption spectra is analyzed. Within density functional tight-binding and line group symmetry based approach it is shown that strain can generate the gap closing in the SC tubes and also substantial changes in the optical conductivity over wide energy range. In particular, absorption spectra of the semi-metallic and narrow band gap SC coils are extremely sensitive to the uniaxial strain.

Thus, rather wide spectrum, up to the highest optical frequencies can be absorbed by an ensemble of the HCCNTs having only slightly different coil parameters. These startling properties of CNCs imply their potential applications as electromagnetic absorbers and optically-based tactile sensors with highly sensitive discriminatory abilities.

# Poster session II



# RELATION BETWEEN STRUCTURE AND PHONONS IN INDIVIDUAL SINGLE- AND DOUBLE-WALLED CARBON NANOTUBES

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We study the phonons of individual suspended single- and double-walled carbon nanotubes by a combination of Raman spectroscopy, electron diffraction and high-resolution electron microscopy.

In a first part, we examine further diameter dependence of radial-breathing like modes of individual suspended single-walled nanotubes and argue over the correctness of the power laws existing in the literature.

In a second part, we analyze the behavior of the radial-breathing like modes (RBLM) and G-modes in more than 13 double-walled carbon nanotubes (DWCNT) on a wide range of excitation wavelengths: 458, 488, 514, 530, 568-633, 647 and 676 nm. We present the excitation profile of RBLMs and G-modes in several DWCNTs. We observe new examples of mechanical coupling between the layers of DWCNTs, which was first reported in [1]. This coupling leads to the appearance of collective vibrations which frequencies are different from ones of RBMs of constituent layers. Due to the mechanical coupling, radial breathing-like modes may be observed whenever only one of the layers is in resonance with the laser energy.

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# Factor-group analysis of Raman–active modes of single-walled carbon nanotubes

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Group theory is a powerful and convenient tool for predicting and explaining Raman spectra of different materials including single-walled carbon nanotubes (SWCNT). Exact classification of SWCNT vibrational modes from those in a graphene is important in predicting their properties. According to the results of factor-group analysis of achiral SWCNTs [1], the number of their Raman-active modes is 8: $2A_{1g}$, $3E_{1g}$, $3E_{2g}$ and $2A_{1g}$, $2E_{1g}$, $4E_{2g}$ for zigzag and armchair SWCNTs, respectively.

We develop the traditional theory of the Brillouin zone folding [2] of the graphene sheet with the aim to establish the correlations between phonon modes in a graphene and SWCNTs. For this purpose we constructed the representations of SWCNTs point groups using the basis functions which are symmetrical coordinates of atomic displacements in the graphene layer. We found the correlation between 4 irreducible representations of graphene layer symmetry group and the $\kappa=0$ optical modes of the rolled SWCNT. All Raman-active vibrational modes in SWCNTs of various symmetry types ($A_{1g}$, $E_{1g}$ and $E_{2g}$ in achiral tubes and $A_1$, $E_1$, $E_2$ in chiral ones) originating from different points of graphene layer Brillouin zone were determined and analyzed. It is important to outline that all Raman–active modes originate from phonons corresponding to the points belonging to the vicinity of the Brillouin zone center.

It is shown that the frequencies of modes originated from acoustic modes of graphene depend on SWCNT indices. The proposed method can be applied for SWCNT chiral-index assignment using polarized Raman scattering data obtained for particular zone-center modes in crossed-polarized and parallel-polarized scattering geometries.

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# THE DEPENDENCE OF GRAPHENE GROWTH ON CRYSTAL ORIENTATION OF THE CATALYST SURFACE

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Graphene has attracted significant interest in recent years due to its unique physical properties. One of the most promising graphene synthesis techniques for further industrial applications is chemical vapor deposition (CVD) because it yields, potentially, high-quality large-area films. Up to now the major attention in the field of CVD synthesis of graphene is paid to its growth on Ni and Cu, though some articles show the possibilities of graphene formation with use of other metals as catalytically active substrate. Still, the correlation between the catalyst surface crystallography orientation and the quality of produced product is not completely understood. Also it is possible that some metals other than Cu and Ni could be utilized for more efficient graphene growth.

The graphene formation process is governed essentially by carbon solubility in substrate material and lattice matching of the substrate and graphene. In the present work the solubility was estimated using carbon-metal phase diagrams (which also helped to estimate the best synthesis temperature) while the lattice matching was simulated using specially created computer program. The combination of solubility and crystallographic data was used to predict whether a given metal with the given surface orientation will be suitable for graphene growth or not.

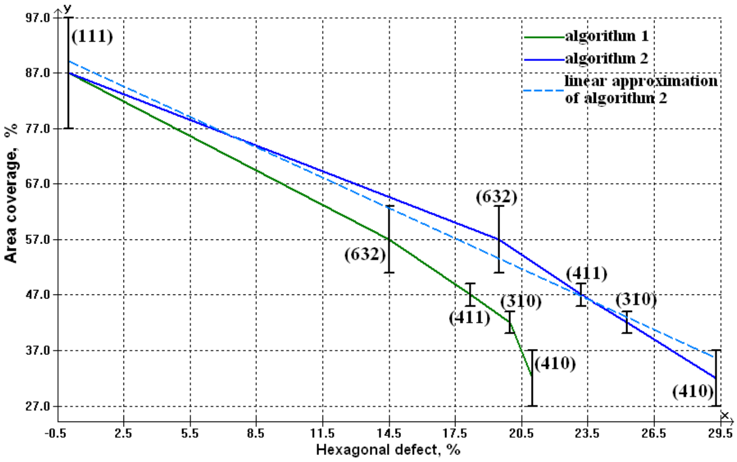

**Figure 1. Correlation between the experiment and the computer simulation.**

Our computer simulation demonstrates good agreement with experiment [1], see figure 1. It was shown that Cu and Ni (in orientations (111), (322) and (433)) are indeed appropriate substrates for the synthesis of graphene by precipitation. Also it is predicted that one of the most promising substrates for graphene growth may be Fe. It combines both good crystallographic matching of (111) and high (111) percentage surfaces to graphene and low carbon solubility. The graphene synthesis could be performed at temperatures as low as 600-700°C. Moreover Fe is a cheap abundant chemically active material that could be easily etched away during the transfer procedure.

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# CHEMICAL VAPOR DEPOSITION OF NANODIAMOND FILMS

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The diamond nanostructures were produced using a Hot Filament Chemical Vapor Deposition (CVD) technique. Parameters of the CVD process were adjusted to provide carbon condensation from the activated methane-hydrogen gas mixture in form of nanocarbon films with predominantly diamond-type atomic structure. Structural and morphological characteristics of the nanodiamond films were obtained by Raman spectroscopy and scanning electron microscopy (SEM) [1–2].

The uniform nanodiamond CVD films were obtained on silicon wafer substrates in diameter up to 150 mm. The nanodiamond deposition has been demonstrated for both single- and poly-crystalline silicon wafers. The elaborated technology is compatible with the standard microelectronic industrial technologies and may be applied for diamond deposition on Si chips with microelectronic architectures.

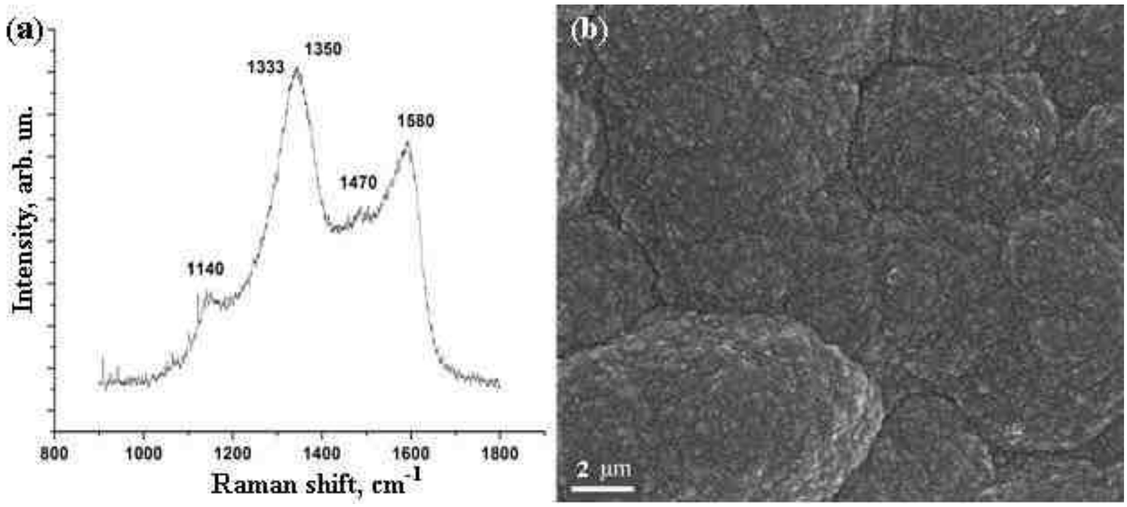

Fig. 1. Typical Raman spectrum(a) and SEM(b) image of nanodiamond film

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# NANO-GRAPHITE-DIAMOND-LIKE MATERIALS FABRICATION WITH LOW PRESSURE NON-EQUILIBRIUM MICROWAVE GAS DISCHARGE AND ITS FIELD EMISSION PROPERTIES

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Application of nano-diamond layers for stable and low voltage auto-emission cathodes for flat panel and vacuum microwave (MW) electronics is considered promising approach [1]. The major advantages of diamond are high carriers mobility and high breakdown strength (avalanche breakdown starts from electric field of 2.2 $*10^7$ V/cm while silicon has just $3*10^5$ V/cm) along with high heat conductivity (2000 W/m*K that five times exceeds values for copper). Such properties allow electron emission generation with high voltage and high currents without concern of cathode damage.

Presented works are targeted for finding the optimal conditions of nano-diamond layers MW deposition process and study of fabricated nano-diamond films emitting properties. Low pressure ethanol non-equilibrium gaseous MW discharge properties were studied for their impact upon self-assembly of nano-crystalline diamond clusters embedded into graphite and polymer-like films. Carbon based nano-structured films were fabricated and possibility of their properties control was demonstrated. It was demonstrated that process can provide a control of diamond nano-cluster's surface concentration within the range from $0.05*10^8$ $cm^{-2}$ up to $1.4*10^8$ $cm^{-2}$ and cluster's linear dimensions within the range 10 – 120 nm [2, 3].

Correlation of diamond-graphite films crystalline nanostructure, film component phase ratio and electron transport and field emission mechanism was studied. Fabricated with nano-graphite-diamond-like cathodes integrated diode array samples demonstrated emission current density up to 2.0 $A/cm^2$. Applied voltage was within the 5-10 V, that provided electric field about 1.5 – 5.0 V/μm for vertical integrated diode design. For lateral emitters emission current density of 20 $A/cm^2$ was obtained with 300V voltage applied.

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# SYNTHESIS OF BORON NITRIDE INITIATED BY MICROWAVE DISCHARGE IN TI—B POWDER IN NITROGEN

G. M. Batanov, N. K. Berezhetskaya, V. D. Borzosekov, E. A. Vasil'eva,
L. D. Iskhakova, L. V. Kolik, E. M. Konchekov, N. K. Kharchev, A. A. Letunov,
D. V. Malakhov, E. D. Obraztsova, E. A. Obraztsova, A. E. Petrov, K. A. Sarksyan,
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Microwave discharge was initiated in Ti—B mixture in nitrogen atmosphere at radiation intensities up to 8 kW/cm$^2$ (wavelength 4 mm, pulse duration 1—4 ms). To the difference of [1], the volume containing the powders was not in any way limited. The space concentration of Ti was of 10 and 20%, respectively.

To the difference of experiments in [2], the open surface of the powders in nitrogen at atmospheric pressure allowed free vaporization of the reaction products and their free gas dynamics spread into the reactor volume.

It was found that the threshold radiation intensity for discharge initiation in such mixtures is about 5 kW/cm$^2$. For mixtures with 10% Ti content, the delay of the discharge development is unstable and reaches 4 ms at radiation intensity 8 kW/cm$^2$. For mixtures with 20% Ti, the delay is 0.4—1.5 ms and decreases with the increase of radiation intensity and duration of irradiation by repeated pulses.

The integral over the spectrum discharge glow increases during the microwave pulse and relaxes after its end with a characteristic time of 0.5 ms for mixtures with 10% Ti and 1.5—2 ms for mixtures with 20% Ti. For mixtures with 20% Ti content, the glow is still present in the reactor volume 40—80 ms after the end of the microwave pulse. This indicates the initiation of the reaction of synthesis of titanium diboride in the powder mixture [1]. The same delayed glow is recorded in 30 following discharges indicating that only a partial burn-out of titanium takes place during a single discharge.

The sputtering of reaction products onto the quartz walls of the reactor as a result of gas dynamic spread of the reaction products was recorded after 10 discharges which followed each other with an interval of 20—60 s. With the use of the Raman scattering method it was proved the creation of boron nitride in mixtures with 20% Ti, and its absence in case of samples with 10% Ti. Thus, it is shown that to produce boron nitride, it is necessary to ignite the long-lasting (40—80 ms) process of synthesis of titanium diboride.

Spectral measurements conducted both at the discharge stage of the process and at the radiation decay stage show the existence of broad spectra consisting of separate atomic lines, molecular bands and continuous background in the range 0.35—0.80 μm.

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# CHEMICAL VAPOR DEPOSITION OF GRAPHENE ON COPPER SUBSTRATES

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Graphene is one of the most interesting materials for researchers during last 5 years. This is due to its electronic structure, which manifested itself in various fields of physics. A demand for the large-scale and high-quality graphene increases with the expansion of the horizons for practical application of this nanomaterial. The production of graphene in the industrial scale remains an open question despite a variety of the synthesis methods developed.

A lot of researchers came to the conclusion that the most appropriate method for this purpose is a chemical vapor deposition of graphene on copper substrates [2]. The number of graphene layers and its quality could be controlled by variation of the synthesis parameters [1]. In this paper we describe the particularities of CVD synthesis of graphene on copper substrates.

One of the differences between copper and nickel (two of the most popular substrates for the graphene synthesis) is a difference in more than 1000 times a carbon solubility in copper and nickel. This means, that with copper the carbon atoms demonstrate no diffusion into the bulk of the substrate, while graphene starts to form onto the surface. The graphene layers formed on the surface of copper were shown to increase in the lateral size and to coalesce into one large area with the time. By varying the growth parameters such as a pressure and concentration of methane, a maximum temperature of the substrate during the synthesis and a cooling rate, we can obtain the samples with the different covering area and the layer number. After several series of experiments the critical parameters have been found for obtaining the maximum area of the graphene sheet with one atom thickness.

*The work was supported by RFBR 10-02-00792 and FP7 IRSES 247007 projects.*

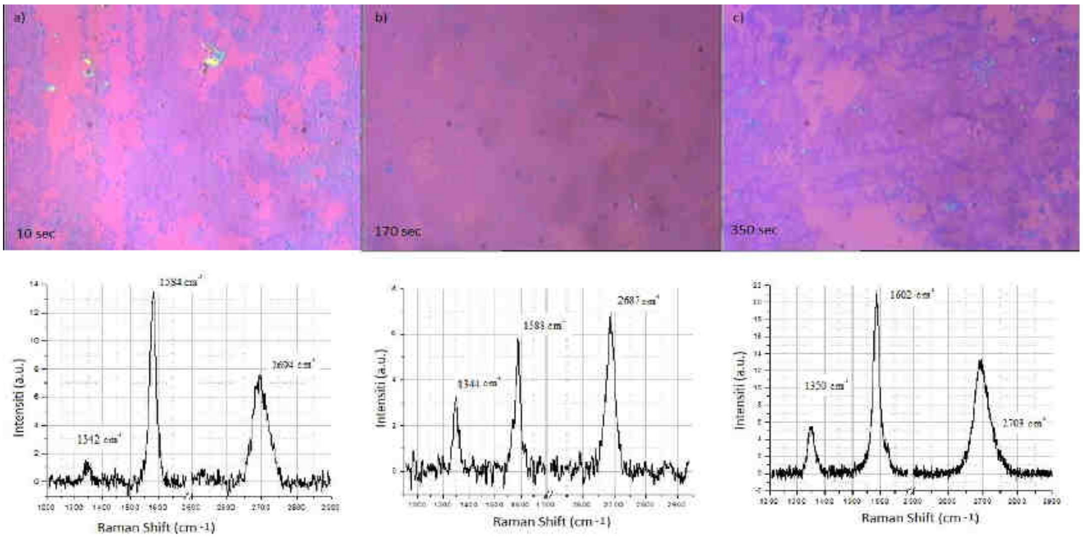

Fig. 1 A dependence of the sample quality on the cooling time. The other parameters were fixed.

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# ON MODELLING OF ULTRAFAST ELECTRON EMISSION FROM CARBON NANOFLAKES.

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Electron emission cathodes are significant devices for various applications in vacuum electronics. Rapid progress in the development of short-pulse electron sources opens up new possibilities in science and technology. Ultrafast electron diffraction [1] and ultrafast electron microscopy [2] are limited to the electron pulse duration. Ultrafast x- ray sources [3] and ultrafast electron crystallography [1] are also requires huge current densities at significantly small emission pulse power. Conventional thermionic and field-emission (FE) electron sources cannot produce required length of electron pulses. The ultrafast electron sources commonly bases on amplified femtosecond lasers focused onto surface of the emitter. We demonstrate ultrafast strong electron emission from nano-graphite field emission cathode under irradiation by femtosecond laser pulses in comparatively low electric field. Emitted charge up to 13 nC/cm$^2$ was observed under irradiation by 55 fs 6 mJ/cm$^2$ pulses at 1 V/μm extraction voltage.

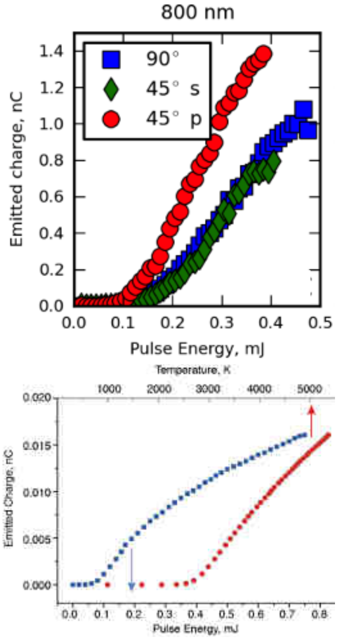

Fig. 1 (upper plate) The measured emitted charge as a function of the pulse energy for different polarizations. (lower plate) The pulse energy dependence of the emission charge calculated in the two-temperature model framework.

High emission intensity of graphite flakes with initially low intrinsic carriers concentration can be described in the frames of two-temperature model. As opposed to standard model that is used to describe metals implementation of two-temperature model for graphite flakes requires consideration of two parallel channel of laser power absorption: generation of free carriers and heating of generated carrier gas. The first channel dominates at the pulse frontier but as the saturation of free carrier generation increases [4] the second channel starts to dominate. The heat capacity of electron gas system may be defined via integral over energy distribution function. Increase of electron gas temperature up to 5000 K (see fig. 1 *down*) gives rise to thermionic emission. The emitted electron cloud drifts from cathode to anode in the extraction field. Recent experiments showed that part of emitted electrons falls back to cathode due to Coulumb repulsion as already emitted electrons form an energy barrier for newly emitted. To simulate the electron cloud drift PIC (Particle In a Cell) code was used. The calculated emitted charge and electron temperature are shown in the fig. 1 *down.* The obtained model describes electron emission stimulated by femtosecond high power laser pulses.

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# FIELD EMISSION PROPERTIES OF SINGLE WALL CARBON NANOTUBE FILMS

Ivan V. Obronov[1,*], Anton Anisimov[3], Brad Aitchison 1[3], Viktor I.Klesch[1], Albert G. Nasibulin[4], Esko I. Kauppinen[4], Alexander N. Obraztsov[1,2]

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The field emission properties of the films of single wall carbon nanotubes (CNT) were investigated for the films of different thickness. The CNT films were produced by an aerosol method and consist of individual nanotubes having typical length of 1-2 µm and diameter of 10-20 nm (see Fig. 1). The individual CNT are joined into bundles randomly oriented in the films with different thickness depending on deposition time duration. The correlation of the field emission (FE) properties with the CNT film thickness was experimentally investigated. We found linear relationship between the CNT film thickness and field emission threshold, current and emission sites density (see Fig. 2). We propose empirical models explaining observed correlation by increase of emission sites density and CNT percolation with the film thickness.

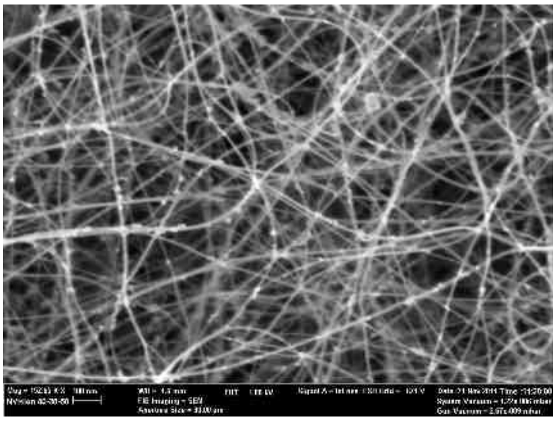
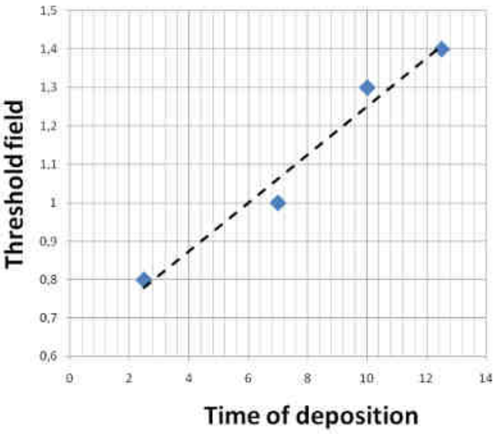


Fig. 1 Typical SEM image of the CNT film



.Fig. 2 Dependence of field emission threshold on deposition time duration

Acknowledgments
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# OPTOELECTRONIC PROPERTIES OF DIAMOND MATERIALS

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We report a study of the optoelectronic properties of micro and nanodiamond materials, including nanodiamond and microdiamond thin films, and single diamond pyramid shaped microcrystallites [1]. The films were obtained by the hot-filament chemical vapor deposition method (HFCVD) and the microdiamond crystallites were obtained by the plasma enhanced chemical vapor deposition method (PECVD) [2]. The topology and surface structure of samples were examined by scanning electron microscopy (Fig.1) and Raman spectroscopy.

The effect of ultraviolet light irradiation produced by deuterium lamp on conductivity and field emission properties of the diamond materials was investigated. The nano- and micro-crystalline diamond films showed significant increase of their electrical conductivity under the UV irradiation. The picoamps photostimulated currents were observed for the diamond pyramids which have no conductivity without irradiation. The light absorbance and photoluminescence spectroscopy were used to establish electronic characteristics of these materials. We propose and discuss possible mechanisms responsible for the field electron emission and photostimulated electrical conductivity of the diamonds.

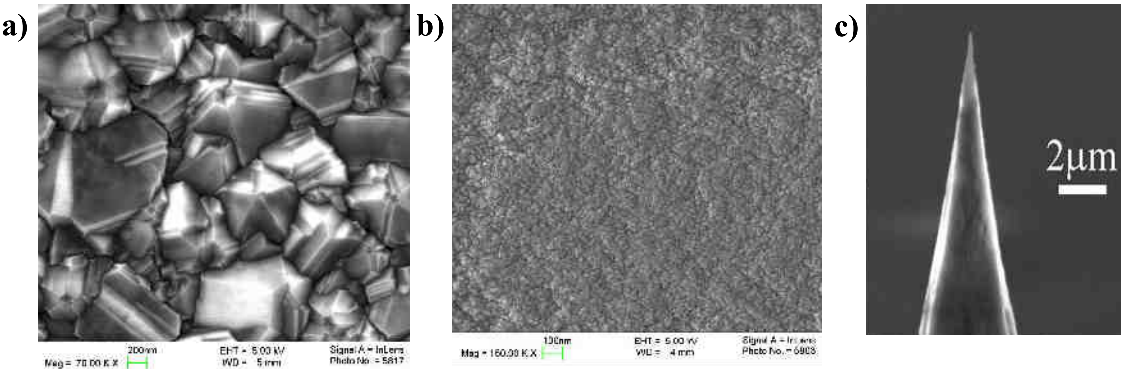

Fig.1. Scanning electron microscopy images of (a) micro- and (b) nanodiamond film, and (c) diamond pyramid shaped microcrystallite.

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# CHARACTERISATION OF NANOCARBON FILMS USING SCANNING FIELD EMISSION MICROSCOPY

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A comparative study of field emission (FE) from various nanocarbon films is presented. The experiments were carried out using scanning anode field emission microscope which was designed to obtain the distribution of field emitters with a spatial resolution of about 1 μm with the scanning area of 1x1 mm$^2$. The scanning anode was made of a tungsten wire and had an opportunity to move within 50 μm range in the direction perpendicular to the film with a resolution of about 1 nm. The diameter of the anode tip was about 1 μm. The FE current dependencies vs. applied voltage, anode vertical position and other experimental parameters were measured during scanning.

The studied materials included films consisting of entangled single-wall carbon nanotubes, obtained by a novel aerosol method [1] (the samples for these investigations were supplied by Dr. A. Nasibulin from Aalto University), and nanographite films consisting of the few-layer graphene (FLG) flakes obtained by a CVD method [2]. It was found that the emission sites distribution and characteristics of individual sites depend on the type and thickness of the films. The possible reasons for the observed differences are discussed.

The planar CVD graphite thin films deposited on dielectric glass substrates were examined by SAFEM. It was found that high density FE current may be observed from the edge of graphite layers. The possible mechanisms of the emission from planar graphite emitters and prospects of their application in vacuum electronics are discussed.

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# FIELD EMISSION PROPERTIES OF CATHODES FROM ALIGNED CARBON NANOTUBE COLUMNES

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Problem of field emission from carbon nanotubes (CNTs) cathodes is a screening of the electric field in the inner regions of the arrays. It is necessary to create a sparse structure or islands from CNTs on the surface of conductive substrate to achieve uniform field emission from the oriented carbon nanotubes array. The traditional solution of this problem is to use the optical and electron-beam lithography to paint the catalyst film which should be used for CNT growth. Since lithography is a complex process that requires specific hardware, we used the simple technique of applying the layer from 70 μm polystyrene balls on cathode surface. Just only one layer of the balls was placed on the substrate surface with a packing close to hexagonal. Then the film of passivator metal (copper) with thickness of ~ 0.1 μm was deposited using the method of thermal vacuum spraying. After that balls were removed and copper mesh with silicon surface areas diameter of 70 μm was obtained. The aligned CNT columns were grown on copper-free silicon arias by aerosol assistant catalytic chemical vapour deposition (CVD) method. The 2% solution of ferrocene in toluene was decomposed on silicon substrate of size 10×10 $mm^2$ at 800°C.

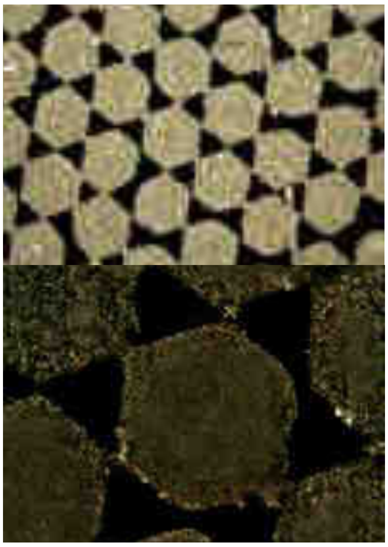
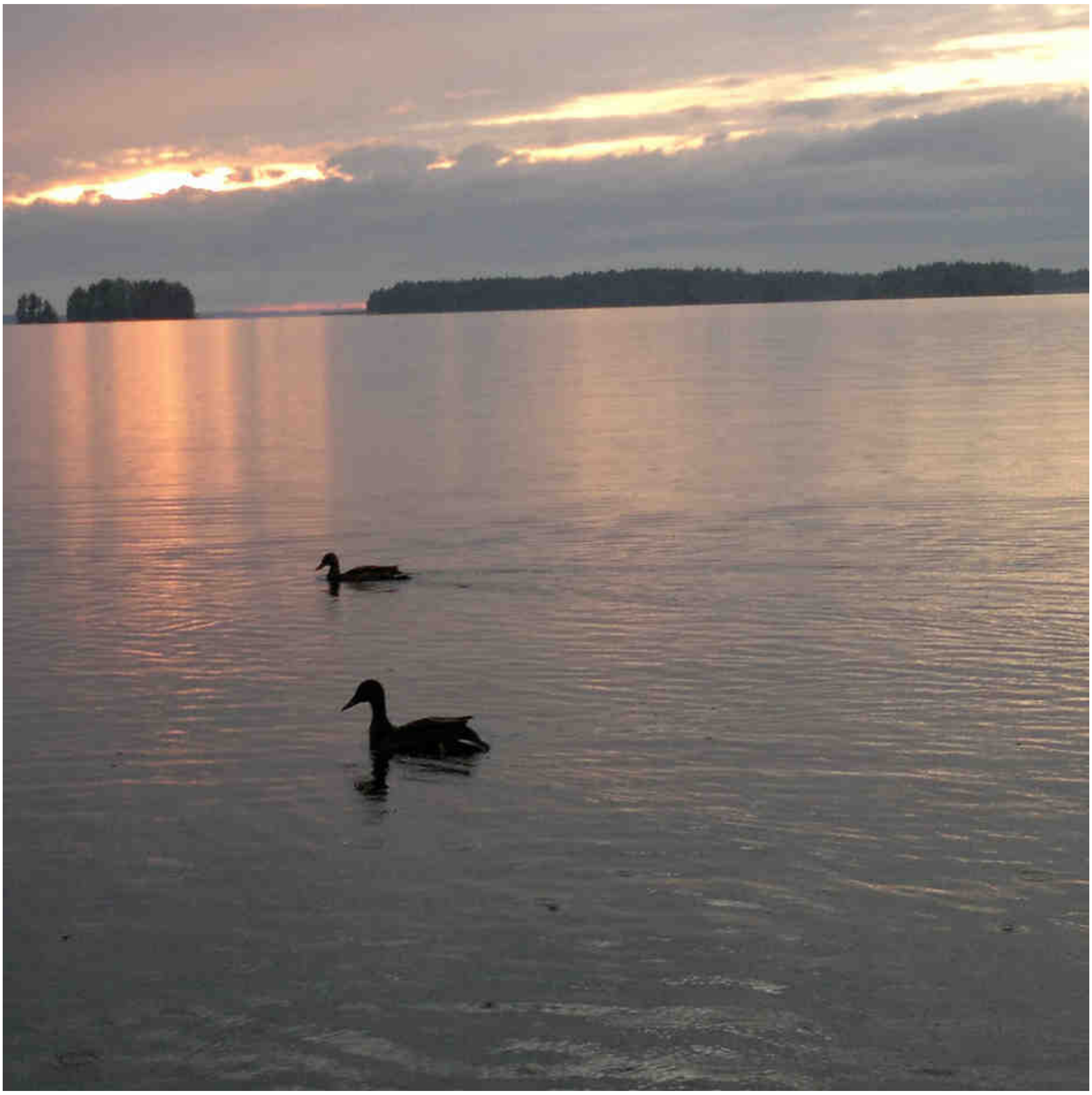


Fig. 1. Columns of oriented carbon nanotubes (diameter 70 μm).

The resulting samples were examined by optical and scanning electron microscopy. The optical image of columns from oriented CNTs with length of 50 μm is shown in Fig. 1. The field emission (FE) properties of the CNT column cathode were measured in the diode regime. The current–voltage (*I*–*V*) dependencies were obtained by varying the applied voltage. Sawtooth voltage up to 1500 V regulated the electric field with frequency ranged from 0.05 to 10 Hz. The inter-electrode distance was varied from 200 μm to 1000 μm. Analysis of *I*–*V* characteristics demonstrated a hysteresis for increasing and decreasing voltage, FE threshold was determined at 1.5 V/μ and more uniform distribution of emission centres was found in comparison with traditional carbon nanotube arrays.

This work was supported by the Russian Foundation for Basic Research, grant 12-02-90011.

# Friday, August 3



# SWCNT CVD GROWTH AND DRY DEPOSITION FOR THIN FILM APPLICATIONS

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We start by reviewing the recent progress in the field of chirality controlled synthesis of SWCNTs by chemical vapor deposition, both supported and floating catalyst methods. Then we present our recent results on SWCNT direct, dry deposition from the floating catalyst reactor at ambient temperature and pressure to manufacture transparent thin film conductors and field effect transistors (TFT). Flexible SWCNT-PET conducting films show transparency-sheet resistance properties similar to those of ITO-PET films. SWCNT network TFTs on both silicon as well as polymeric substrates show mobilities of 35 cm2/Vs and on/off ratio of 5*106. Also, we developed free standing SWCNT films for various applications.

To further control the tube properties, we have carried out studies on SWCNT growth from carbon monoxide (CO) using supported CVD methods. When using supported bimetallic Fe-Cu catalysts, very narrow chiral distribution SWCNTs were produced. In addition, epitaxial formation of cobalt (Co) nanoparticles via $Co_xMg_{1-x}O$ solid solution reduction in CO enables to grow SWNTs with a narrow diameter distribution. *In situ* environmental $C_s$-corrected transmission electron microscopy (ETEM) studies reveal that the Co nanoparticles remain in metallic state and their epitaxial contact with MgO support remains coherent during SWNT growth process.

# IODINE INTERCALATION FOR CONDUCTIVITY IMPROVEMENT OF SINGLE-WALL CARBON NANOTUBE FILMS

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Single-wall carbon nanotubes (SWNTs) still attract a huge interest due to a great set of unique properties promissing for different fields of science and technology. In the present work, we study transparent, conductive iodine-doped SWNT films in comparison with the indium tin oxide (ITO) and graphene films.

The SWCNT films have been grown by aerosol-CVD method [1]. A vapor phase iodination was used [2]. Films constituted from SWNTs with diameters from 1.3 to 2.0 nm have been placed into the chemical glass cell together with the iodine crystals and heated up to 130 – 150°C. The process lasted 12 hours. Afterwards the samples were cooled down to 50-60°C during 2-4 hours.

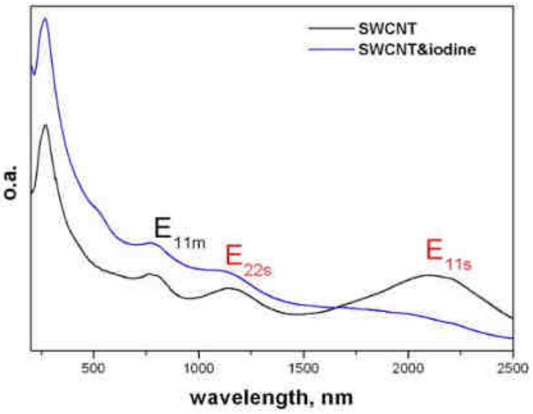

Fig.1. The optical absorption spectra of the raw and iodine-doped SWCNT films.

The efficiency of intercalation has been estimated by optical absorption and Raman spectroscopy. The absorption spectra have shown that semiconductor SWCNTs have changed their properties to metal ones. This fact has been confirmed by a suppression of the first electron transition for semiconductor SWCNTs in UV-vis-NIR optical absorption spectra (Fig.1). After the iodine treatment the sheet resistance of SWCNT-films has been decreased by an order of magnitude (from 1550 Ohm/sq to 270 Ohm/sq at room temperature). This difference could be increased via additional densification and functionalization of the film.

The obtained data are comparable for the characteristics of ITO and graphene films.

The work was supported by RAS research programs, European project IRSES N247007 and Russian President grant MK-5618.2012.2

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# STRETCHING OF CARBOXYMETHYL CELLULOSE FILMS WITH DISPERSED SINGLE-WALL CARBON NANOTUBES

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Last few years single-wall carbon nanotubes (SWCNTs) have found their place in various fields of applications. SWNTs turned to be very efficient passive mode-lockers for formation of ultra-short laser pulses in near-IR spectral range [1,2]. In Er and Tm fiber lasers the carboxymethyl cellulose (CMC) films were successfully used for formation of sub-picosecond pulses [3,4].

The electrical and optical properties of SWCNTs (conductivity, optical absorption etc.) depend on the nanotube orientation [5, 6]. The alignment of nanotubes in the CMC films could increase sufficiently the efficiency of the last one as non-linear element in laser resonators.

Here, we demonstrate the method of the alignment of SWNTs, embedded into a polymer film. The suspensions of SWNTs in 4 wt% CMC water solutions were dried at ambient conditions during 4-5 days. The obtained films were flexible because they still contained some amount of water. The films were stretched in a chosen direction. The ratio of the obtained and the initial length was up to 6. As a consequence, SWNTs were aligned parallel to this direction. The polarised Raman intensity dependencies (shown in Fig.1.) demonstrate a strong anisotropic behaviour.

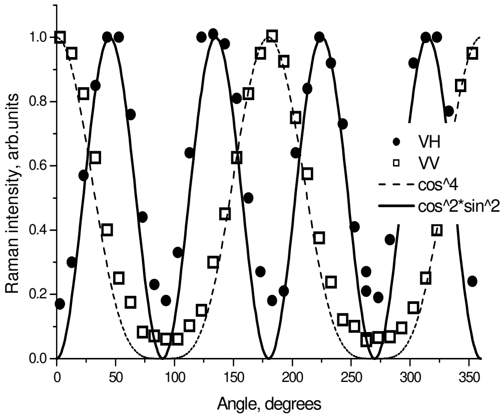

Fig.1. A polarization dependence of the intensity of Raman mode at 1592 $cm^{-1}$ in crossed (VH) and parallel (VV) configurations of the registration.

*This work was supported by the federal target program "Scientific and pedagogic personnel of innovative Russia" 2009-2013, contract П1286, Grant of Russian President MK-2164.2011.2 and RAS research programs.*

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# MULTI-WALLED BORON NITRIDE NANOTUBES MODIFICATION BY ALUMINUM ION IMPLANTATION

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Recent progress in boron nitride nanotubes (BNNT) synthesis [1,2] opens new possibilities to use attractive combination of their excellent mechanical characteristics with thermal and chemical stability of this nanomaterial for creation of new structural components and reinforcing fibers. In this work we have applied metal ion implantation technique to prepare BNNT/Al nanocomposites. The resulting structures have been studied using a combination of high-resolution transmission electron microscopy and Raman spectroscopy. According to our data depending on the ions energy a row of structures can be obtained as a result of implantation process: amorphous fibres covered by metallic nanosized particles (in case of high energy ions); BN fibres with a partially preserved crystallinity covered by a uniform metallic layer; BNNT with defects introduced during the ion bombardment process (in case of the comparatively low energy ions) [3]. TEM overview images of the samples before and after Al ion implantation are presented in Figure 1. In the Raman spectra (Fig.2) two peaks are clearly seen: 1366 cm$^{-1}$ band corresponds to in-plane vibrations between B and N atoms; a slightly less intensive and broad feature around 1293 cm$^{-1}$ appears in the highly disordered hexagonal BN samples. This indicates a presence of crystalline and amorphous phases in BNNT samples after implantation.

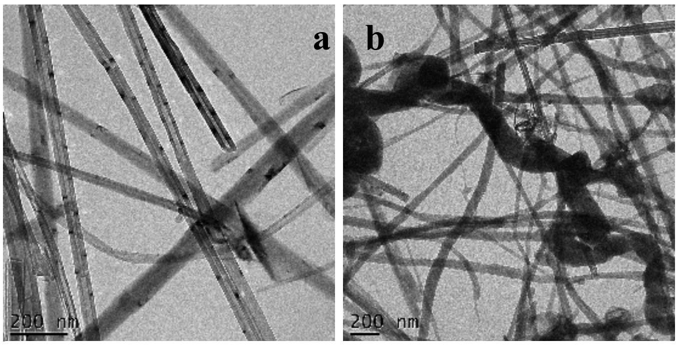

Figure 1. TEM image of a BN nanotubes sample before (a) and after (b) modification by Al ion implantation at 20 kV; 10 mA for 10 min

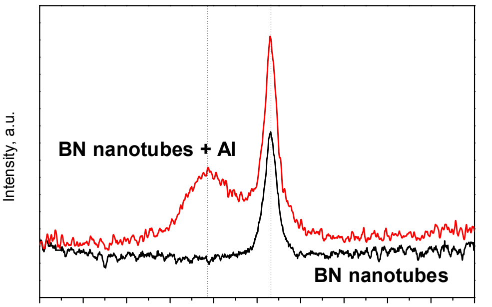

Figure 2. The Raman spectra of the BN nanotubes before (black) and after (red) Al ion implantation.

*Acknowledgements: This work was supported by the Grant of Russian Federation Ministry for Science and Education (grant №11.G34.31.0061).*

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# SEPARATION OF SINGLE-CHIRALITY SINGLE-WALL CARBON NANOTUBES

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It is well known that no production method can control chirality of single-wall carbon nanotubes (SWCNTs) perfectly. Products are always mixture of variety of structures for both metallic (M-) and semiconducting (S-) SWCNTs. This is one of the most serious problems to bring out their extremely high performance in electronic device applications. A way left to get single chirality SWCNTs is the structure sorting after growth, but was thought to be very difficult. In 2006, however, density gradient ultracentrifugation (DGU) technique made a breakthrough to sorting structure of SWCNTs and opened a new research field, “separation of SWCNTs”. [1] It is interesting that DGU has been often used in biology. Because of an analogy in structures between DNA and SWCNTs, it is reasonable that Tanaka tried the gel electrophoresis for the separation of SWCNTs. [2] After these discoveries, DGU and gel separation methods have been competing each other towards more and more precise structure separation. Now we have developed multicolumn gel chromatography method for the precise structure sorting of S-SWCNTs using commercially available Sephacryl gel [3]. Appling this method twice to HiPco SWCNTs, we sorted out 13 kinds of S-SWCNTs by the difference in the local C-C bond curvatures. However, this two-step separation method is too complicated to be applied to the large scale separation. For the further improvements, we have analyzed separation mechanism and then found that it is possible to control the interaction between S-SWCNTs and the Sephacryl gel by changing surfactant concentration and the system temperature. Finally, we succeeded in simplifying the separation procedure and 7 kinds of single chirality S-SWCNTs were sorted out from raw HiPco by a single step multicolumn method. This simple method can be applied to the large scale separation of single chirality SWCNTs. In this presentation, I will show the present and the future perspective of the separation of SWCNTs..

13 kinds of single chirality SWCNTs

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# EFFECTIVE NON-DISTRACTIVE CUTTING OF SINGLE-WALL CARBON NANOTUBES

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A significant progress in purification, functionalization, and cutting of SWNTs has been achieved during last few years. Different methods were developed to decrease SWNT length, such as through fluorination or acid treatment [1], mechanical cutting by intensive ultrasonication [2,3] or ball-milling treatment [4], lithography cutting approach [5] and others. The most simple and frequently used approach is based on refluxing or sonication of SWNTs in a mixture of acids. However, application of these methods resulted either strong SWNTs degradation or strong carbon loss. In present communication we report on the effective non-distractive cutting of SWNT by high power ultrasonication in mixture of sulfuric and nitric acids. The cutting strategy is based on application of the optimized acid concentration (mixture (3:1) of 98% sulfuric and 59% nitric acids) at lower temperature (less than 8 0C). Intensive ultrasonication in acids mixture at low temperature for 30 hours leads to reduction of SWNTs length from 1-2 µm till 50-200 nm with minimal carbon loss and weak disturbance of electronic properties of SWNSs.

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# GRAPHENE SYNTHESIZED BY ATMOSPHERIC PRESSURE CHEMICAL VAPOUR DEPOSITION

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Since the demonstration of potentiality for obtaining a micrometer scale graphene a lot of efforts were performed to develop the method of making a large scale graphene for industry application. Such a strong interest in graphene production is based on the outstanding properties of this 2D material. Current methods to produce graphene involve the mechanical cleavage or chemical exfoliation of graphite, graphitization of silicon carbide surface in ultra-high vacuum, epitaxial growth via Chemical Vapor Deposition (CVD), or the unzipping of CNTs. Mechanically cleaved graphene has already demonstrated a high chemical, thermal and mechanical stability, record value of flexibility, mobility and transmittance. However scotch tape method is applicable only for micrometer size samples.

Recently CVD has proven to be a promising technique due to its low cost and effective production of large scale and high quality graphene onto the surface of different transitional metals (Pd, Pt, Co, Ru, Ir, Ni, Cu). Among the aforementioned candidates, Cu has confirmed the robustness of this technique due to the self-limitation mechanism of the Cu surface for the fabrication and growth of one layer graphene.

Our investigation is concentrated on the growth of graphene by atmospheric pressure CVD (APCVD). This CVD set-up is technologically more attractive for large scale production of graphene because it is inexpensive and readily accessible way for the growth of reasonably high quality graphene. Most of the successful results in obtaining high quality graphene were realized using the APCVD growth from methane and hydrogen gas mixture on the Cu foils. We showed that using ethylene as a source of carbon lead to time reducing of the graphene formation up to a few seconds. Another promising approach is to use metal films heteroepitaxially deposited on conventional single crystalline substrates. Our proposed route of making graphene is based on the combination of plasma vapor deposition (PVD) and the APCVD synthesis. PVD technique we used to tailor the catalysts were successfully modified to deposit a single crystal Cu (111) film on c-plane sapphire. Moreover, sputtering route of catalyst preparation allows us to control the size and the shape of graphene films deposited on it. Additionally after the APCVD graphene growth on such samples it is easier to transfer as-produced film to alternative substrates by wet-etching of the Cu catalyst.

# PRECISELY CONTROLLED CVD SYNTHESIS OF GRAPHENE

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Graphene is one of the most interesting carbon nanomaterials. It is a two-dimensional hexagonal lattice of carbon atoms. The chemical vapour deposition method from a carbon containing gas for growth of the pyrolytic graphite on nickel was used more than 20 years ago. But only 4 years ago this method has been employed for growth of a single graphene layer [1].

In this work we demonstrate the hand-made installation for graphene synthesis by chemical vapour deposition on the nickel foil from a gas mixture of methane and hydrogen [2]. We present an accurate and detailed description of the growth process of the graphene films with different thickness on the nickel foils of 25 µm thickness. There are several main parameters of the process: a pressure in the chamber, a concentration of methane in the gas mixture and a maximum temperature of the substrate during the synthesis.

The real time controlled synthesis is demonstrated in this work. We heated the metal foil via Joel effect with a direct input of the high current and measured the resistance of the foil during the experiment. After the injection of the methane in the chamber the heating of the substrate starts. The resistance increased linearly with increasing the temperature. But when the temperature of the nickel foil reached the certain value, the rate of the stance increasing had chaged see Fig. 1). This turning point was interpreted as a moment of the beginning of the carbon diffusion inside nickel. Thereby the amount of diffused carbon may be estimated from a difference between the maximum temperature of the substrate and the temperature when the diffusion started. It also depended on the pressure in the chamber and on the concentration of methane. As a result we controlled the thickness of graphene film by controlling the amount of diffused carbon.

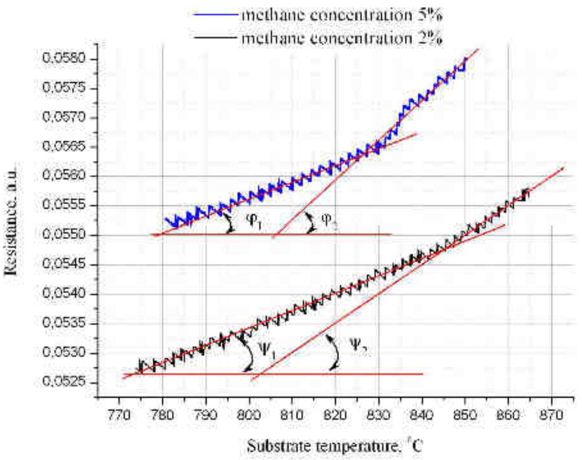

*Fig. 1. A dependence of the resistance of nickel foil on the foil temperature.*

The synthesised samples were characterized by the Raman spectroscopy, the optical absorption spectroscopy and the scanning electron microscopy. They have confirmed a presence of the single graphene layer.

*The work was supported by RFBR 10-02-00792 and 11-02-92121 and “Umnik” project.*

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# CHARACTERIZATION OF CARBON NANOTUBES GROWN DIRECTLY IN A FIELD EMISSION ELECTRON MICROSCOPE

Alina Pascale*, Sorin Perisanu*, Arnaud Derouet*, Anthony Ayari*, Philipppe Poncharal*, Pascal Vincent*, Catherine Journet‡ and Stephen Purcell*

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We have recently shown that individual single wall carbon nanotubes (CNTs) can be grown on metallic tips in a field emission microscope (FEM) which allows direct observation from the nucleation stage till the end of the growth [1]. In this talk I will review our progress with this synthesis method and discuss the comportment of the as-grown CNTs as field emission sources and nano-mechanical oscillators.

The growths are carried out in extremely low pressures of $\sim 10^{-7}$ Torr of acetylene which gives the lowest recorded growth rates of ~0.05 nm/sec and the possibility of interactive control of the growth rate by varying the pressure and temperature. The most notable fact is that the CNTs most often rotate axially during their growth, thus supporting a proposed 'screw-dislocation-like' (SDL) model [2]. Detailed analysis shows that we directly observe the insertion of individual carbon dimers at the CNT base [1] which causes a rotation of the CNTs and corresponding FE patterns. The growths tend to terminate abruptly likely due to catalyst poisoning when the nanotubes are in the 30-200 nm range. The CNTs on tips are quite unique as mechanical oscillators and field emission sources.

The mechanical resonances of these singly clamped nanotubes can be measured directly in-situ by observing the enlargement of the FE pattern when in resonance [3]. Vibration frequencies $\upsilon_0$ up to 2 GHz and estimated Q factors up to 25800 have been measured at room temperature [3]. These CNTs have the largest mechanical figure of merit M, defined as $M = Q\upsilon_0/V$ at room T where V is the volume of the cantilever.

FE voltages as low as 80 Volts and FE currents up to 3 μA can be achieved, the later appearing to be a record for SWNTs. Interestingly, we observe clear evidence of the influence of Coulomb blockade on the I(V) characteristics depending on the CNT length.

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# SCANNING ANODE FIELD EMISSION MICROSCOPY OF NANOCARBONS

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Field emission (FE) properties of various nanocarbon materials have been examined using a scanning anode field emission microscopy (SAFEM) technique. The scanning anode was made of a tungsten wire with micron sized tip. The anode had an ability to scan the area of 1x1mm$^2$ and move in vertical direction in the range of 50 µm. The FE properties were examined with voltage applied between the nanocarbon sample and the anode. The FE current dependencies vs. applied voltage and other parameters of the FE obtained during scanning were analyzed and compared for different nanocarbons.

The materials examined included films consisting of entangled single-wall carbon nanotubes (SWNTs) obtained by an aerosol method [1] (the samples for these investigations were supplied by Dr. A. Nasibulin from Aalto University) and nanographite films consisting of the few-layer graphene (FLG) flakes obtained by a CVD method [2]. The flakes have predominant orientation perpendicularly to the flat Si substrates. The FE properties of the films prepared with different parameters of the synthesis processes were examined. Obtained data revealed that there is clear correlation of the current density and emission cites distribution depending on the type and thickness of the film. The possible reasons for the observed differences are discussed. The FE degradation of individual emission cites at high emission currents has been investigated in other experiments where FE parameters, at which the destruction of individual emission sites occurred, were determined. Using obtained data the maximum average current for the multiemitter FE cathodes consisting of tip-like emitters was estimated to be in the range of 1-10 A/cm$^2$.

The FE properties of the planar CVD thin graphite films deposited on dielectric glass substrates were investigate using the SAFEM technique. A high density stable FE current was detected from the edge of the graphite film. The stability and maximal value of the FE currents were determined experimentally. The possible mechanisms of the emission from planar graphite emitters and prospects of their application in vacuum electronics are discussed.

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# OPTICAL STUDY of NANOTUBE and CORONENE COMPOSITES

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SWCNTs are one of the most exciting materials today. They appeared to be extremely useable in various fields of applications. One of the most fascinating methods of utilizing nanotubes is to use them as a template for synthesis of other extraordinary nanomaterials or even as a supporting construction for unique (not existing in the suspended state) nanomaterials. The ultimate mechanical, chemical and physical properties of SWCNTs, basically, their stability upon various stress and a specific quasi-one-dimensional electronic structure and a tunability of their geometry, make them perfect candidates for the above-mentioned area of applications. The novel structures, properly designed in this way, as well as SWNT-based composites would possess unique properties and find a wide variety of applications.

An optical absorption spectroscopy, a photoluminescence spectroscopy and a Raman spectroscopy proved to be the efficient methods to characterize SWNTs. Moreover, in combination these analytical optical methods can be even more efficient, especially for description of SWNT-based composites.

In this work we tried to characterize SWNTs with graphene nanoribbons (GNR) inside using a combination of optical techniques. In order to solve this problem we began with investigation of initial materials. Samples containing SWNT&GNR composites were synthesized mainly from nanotubes with a specific distribution and various forms of coronene molecules. From photoluminescence study SWNTs appeared to be broadly distributed with a considerably large average diameter. The coronene showed a quite intensive photoluminescence in visible spectrum range with a specific profile. A photoluminescence of composites showed peaks similar to ones of coronenes confirming a presence of impurities in the samples (Fig. 1). Therefore, one needs to imply more precise purification method in order to verify the intrinsic properties of SWNT&GNR composite. In order to get the high quality optical measurements a specific preparation of the samples has been done. The other approach is to use a more intense light source. However, at each step the state of the procedures the samples should be monitored, in order not to corrupt the very structure.

After procedures be finalized, thorough analysis of the measurements will be held. These will provide us data to verify the differences and interpret the results.

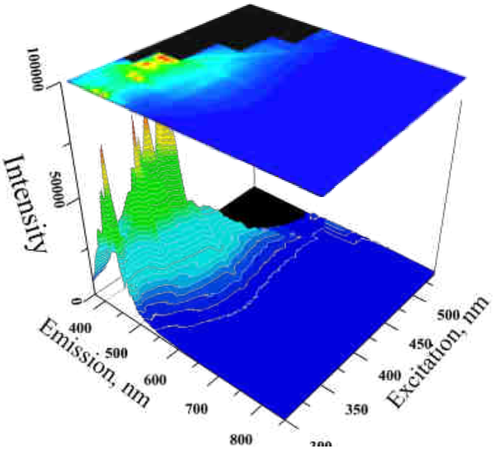

Fig. 1. Photoluminescence excitation map of SWNT@GNR in a visible range.

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# LOW-DIMENSIONAL HYBRIDS FROM CARBON NANOTUBE ARRAY AND MOLYBDENUM DISULPHIDE

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Combination of carbon nanotubes (CNT), possessing high electrical conductivity, with semiconducting nanoparticles allows creating a new class of low-dimensional hybrid materials with unique electronic, optical and luminescent properties. Hexagonal lattices of graphitic materials and molybdenum sulfide $MoS_2$ allow jointing these compounds in a hybrid. There are a few methods proposed to cover nanotubes with $MoS_2$, but all of them are destructive for CNT arrays [1-3]. Preserving the nanotube alignment in a hybrid with $MoS_2$ is important for the materials utilized as field cathodes or anodes in lithium ion batteries [4].

Here we developed approach for creation of hybrid structures based on molybdenum sulphide nanoparticles and aligned CNT arrays. We have proposed a postprocessing of CVD-grown nanotube arrays for the array compacting. Deposition of $MoS_2$ was carried out using thiourea and ammonia molybdate solution in hydrothermal process. The synthesis was performed at 235°C during 24 hours. The samples obtained were examined using optical and scanning electron microscopy, Raman spectroscopy, and x-ray photoelectron spectroscopy. The $MoS_2$ content in sample cross-section was estimated using Raman spectroscopy. The field electron emission from the hybrid sample was compared with those from the uncovered CNT array.

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