Nikolaev Institute of Inorganic Chemistry SB RAS
Boreskov Institute of Catalysis SB RAS
Rzhanov Institute of Semiconductor Physics SB RAS

The 7th Russian-French Workshop on Nanoscience and Nanotechnologies

PROGRAM AND ABSTRACTS BOOK

3–6 June 2013
Novosibirsk, Russia

УДК 546.26 + 54.052 + 537.877

Abstracts of the 7th Russian-French Workshop on Nanoscience and Nanotechnologies/ Responsible editor Alexander V. Okotrub. Novosibirsk: Nikolaev Institute of Inorganic Chemistry SB RAS, 2013, 112 p.

ISBN 978-5-901688-29-8

The first workshop has been held in Moscow (in the Institute of Crystallography RAS) in 2004. It has been initiated by CNRS, RAS and French embassy in Moscow. The following seminars in this series have been held in Lille (France 2005), St. Petersburg (Ioffe Physico-Technical Institute 2006), Autrans (France, 2007), Moscow (GPI, Russia, 2008) and Paris (France, 2010).
Originally, the seminar covered three main fields: teraHertz and middle infrared range electronics, carbon and semiconducting nanostructures, spintronics and nanomagnetism. Starting from 2007, the field "teraHertz and middle infrared range electronics" have been separated into the independent workshop. Instead, a new field "Nanophotonics" has been introduced. This theme has attracted a great interest of participants in 2007 (Autrans, France). Moreover, during last 2-3 years the unique properties of two-dimensional carbon structure - graphene has attracted a lot of attention of scientific community.

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Schedule-at-a-Glance

Day	**Monday, June 3**	**Tuesday, June 4**	**Wednesday June 5**	**Thursday, June 6**
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9:50-10:40	Session “Carbon nanotubes and graphene I”			
10:40-11:00	Coffee & Tea			
11:00-12:40	Session “Carbon nanotubes and graphene II”	Session “Carbon nanotubes and graphene IV”	Session “Nanophotonics II”	Session “Carbon nanotubes and graphene VI” Round Table & Discussion Closing Ceremony
12:40-14:00	Lunch			
14:00-15:40	Session “Semiconductor nanostructures and nanowires I”	Session “Semiconductor nanostructures and nanowires III”	Session “Magnetics and nanomagnetics I”	Excursion to Novosibirsk
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Monday, June 3

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10:15-10:40	**Vladimir Kuznetsov,** *BIC SB RAS, Novosibirsk* Study of the active component formation of Fe-Co catalyst for MWCNT growth by means of *in situ* methods
	Session “Carbon nanotubes and graphene II” (I.V. Antonova)
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Wednesday, June 5

Location: Nikolaev Institute of Inorganic Chemistry SB RAS

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Tamm plasmon laser

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Harnessing light with photonic wires: from needles to trumpets

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Surface Tamm states in two-dimensional photonic crystal made of macroporous silicon

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Thermo/photo-switchable molecular nanomagnets based on copper-nitroxide clusters: an EPR study

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^{129}Xe NMR for porous carbon materials including multi-wall carbon nanotubes

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Thursday, June 6

Location: Nikolaev Institute of Inorganic Chemistry SB RAS

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10:15-10:40	**Olga Sedelnikova,** *NIIC SB RAS, Novosibirsk* *Ab initio* study of electronic and optical properties of defective graphene
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11:50-12:15	**Vladimir Fedin,** *NIIC SB RAS, Novosibirsk* Nanoporous MOFs: host-guest chemistry and material properties
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	Closing Ceremony

Monday, June 3

Understanding the correlation catalyst particles - SWNT diameters in CVD processes

Annick Loiseau

LEM ONERA-CNRS, Chatilon

Study of the active component formation of Fe-Co catalyst for MWCNT growth by means of *in situ* methods

V.L. Kuznetsov[1,2], D.V Krasnikov[1,2], A.N. Shmakov[1,2], O.B. Lapina[1], A.S. Andreev[1,2],
A.V. Ishchenko[1], K.V. Elumeeva[1]

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[2]*Novosibirsk State University, Novosibirsk, Russia*

Multi-walled carbon nanotubes (MWCNTs) are known to be perspective component for many applications due to their unique properties. Their properties mainly depend on the diameter distribution and defect concentration, which, in turn, mainly depend on the catalyst nature and growth conditions. Previously it was demonstrated that the formation of the catalytic species and nucleation of the carbon deposits determine the selectivity and activity of nanotube growth process. Thus, the investigation of the catalyst active component formation is extremely important for the design of selective processes of MWCNT production. In the present work the formation of the active component of the bimetallic Fe-Co catalyst during MWCNT growth was studied using *in situ* synchrotron radiation XRD analysis. The XRD data in combination with the results of other physical methods (HRTEM, internal field ^{59}Co NMR) can be used for the development of kinetic model and the optimization of the synthesis conditions to produce MWCNT with controlled properties in a fluidized bed reactor. Pechini-type method of Fe–Co catalyst production demonstrates much higher MWCNT production with different structural properties than it was described before.

Double-walled carbon nanotubes: the balance between potential impact on health and/or the environment and biomedical applications

E. Flahaut[1], E. Meunier[2], B. Pipy[2], F. Bourdiol[1, 3], F. Mouchet[3], E. Pinelli[3], L. Gauthier[3]

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[2]*Pharma-DEV, UMR 152, Toulouse, France*
[3]*ECOLAB, UMR 5245, Auzeville, France*

The increase in carbon nanotubes (CNTs) production (estimated to reach 14000 tons in 2016) is driven by many applications – many of which being already on the market (paints and composites). In parallel, questions are also raising about their safe handling and use (workers), but also about their end of life in the environment. The CIRIMAT is focusing for 10 years on the CCVD synthesis of double-walled CNTs (DWNTs) [1] because they represent unique objects at the interface between single-wall CNTs (SWNTs) and larger multi-walled CNTs (MWNTs). The protection offered by the outer tube allows to modify the interface with the environment (solvent, matrix, *etc*.) while minimizing interferences with the inner one, and keeping a morphology close to that of SWNTs.

After briefly reminding the most recent results in terms of impact on health (Pharma-DEV) and on the environment (ECOLAB) and discussing the issues of metrics for the comparison of the results as well as the influence of sample processing [2], we will describe our recent advances in the biomedical field and especially in CNT-mediated drug delivery and brain tissue engineering [3].

[1] E. Flahaut, R. Bacsa, A. Peigney, Ch. Laurent, Chem. Commun., (2003), 1442-1443.
[2] F. Bourdiol, F. Mouchet, A. Perrault, I. Fourquaux, L. Datas, C. Gancet, J-C. Boutonnet, E. Pinelli, L. Gauthier, E. Flahaut, *Carbon*, 54, (2013), 175-191.
[3] A. Beduer, F. Seichepine, E. Flahaut, I. Loubinoux, L. Vaysse, Ch. Vieu, Langmuir, 28, (50), (2012), 17363–17371.

Nucleation and growth of carbon nanostructure investigation with nanosecond time resolution by synchrotron radiation methods

B.P. Tolochko

ISSCM SB RAS, Novosibirsk

Carbon nanotube nanostructures: resonance and anti-Stokes Raman effects

S. Lefrant[1] , J.P. Buisson[1], J.Y. Mevellec[1], C. Ewels[1], C. Bergeret[2], J.Cousseau[2],M. Baibarac[3] and I. Baltog[3]

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Raman scattering still plays a major role for the understanding of the electronic properties of carbon nanotubes. In the case of functionalized SWNTs, a systematic study of the Raman response as a function of the excitation wavelength allows to interpret the changes in radial breathing mode frequencies and transition energies for both semiconducting and metallic tubes and demonstrate that the type of chain covalently bound to the tubes plays an important role, notably when oxygen atoms lie close to the tubes, inducing a larger shift in transition energy.

The use of SERS (Surface Enhanced Raman Scattering) recently revealed peculiar properties such as an abnormal anti-Stokes Raman emission. This effect, reminiscent to a Coherent anti-Stokes Raman Scattering (CARS) emission, results from a wave mixing process between the incident laser light and Stokes Raman light, generated by the SERS mechanism. Both resonance and anti-Stokes Raman effects will be discussed in the case of pristine SWNTs and composite materials.

Electronic structure of narrow graphene nanoribbons

A.I. Chernov[1], P.V. Fedotov[1], A.V. Talyzin[2], I.L. Suarez[1], I.V. Anoshkin[3],
A.G. Nasibulin[3], E.I. Kauppinen[3], E.D. Obraztsova[1]

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[2] *Department of Physics, Umeå University, S-90187 Umeå, Sweden*
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Graphene nanoribbons (GNRs) encapsulated in single-walled carbon nanotubes (SWCNTs) were unambiguously identified using photoluminescence (PL) spectroscopy in the samples of GNR@SWCNTs synthesized using confined polymerization and fusion of coronene molecules [1]. The width of the GNRs is below 1.2 nm. Narrowing of the GNR width leads to the opening of the band gap up to 2 eV. Electronic structure of GNRs encapsulated in SWCNTs was studied by Raman and photoluminescence (PL) spectroscopies. New spectral features corresponding to GNRs were detected by PL in the visible range. In the IR range we detect various shifts in emission and excitation depending on the geometry of the nanotubes [2]. Additional components within the 2D line of SWCNTs were identified after the formation of GNRs (Figure 1). Radial breathing modes of GNR@SWCNTs demonstrate significant shifts (up to 10 cm-1) in comparison to pristine SWCNTs.

The work was supported by RFBR grants 13-02-01354, 12-02-31581, RAS research projects and SP-7362.2013.3.

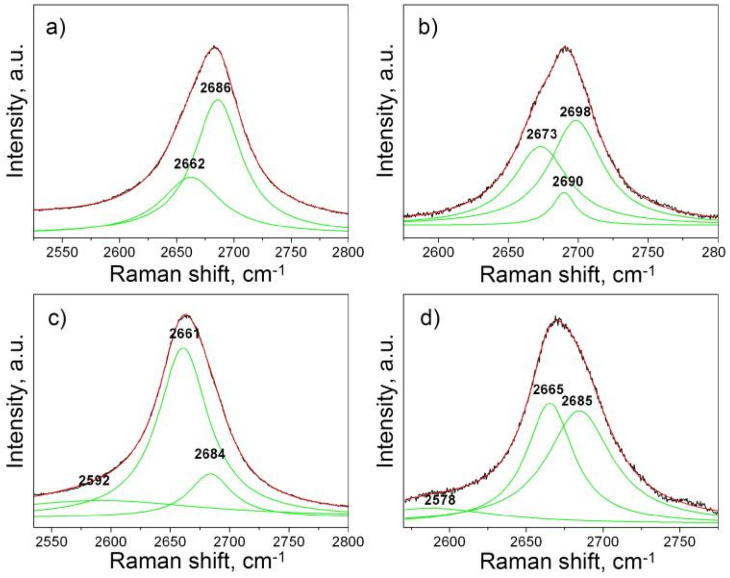

Figure 1 Raman spectra of 2D band of pristine SWCNTs (a,c) and GNR@SWCNTs (b,d) measured with 488 nm excitation wavelength (a,b) and 514 nm (c,d). Fitting lines are in green colour.

[1] A.V. Talyzin, I.V. Anoshkin, A.V. Krasheninnikov et al., *Nano Lett.* 2011, **11**, 4352-4356.
[2] P.V. Fedotov, A.I. Chernov, A.V. Talyzin et al., *J. Nanoelectron. Optoelectron.* 2013, **8**, 16-22

GeSi quantum dot nanostructure: size/space ordering at epitaxy and applications in nanophotonics

A.V. Dvurechenskii
RISP SB RAS, Novosibirsk

The formation of well-defined and ordered semiconductor quantum dot (QD) nanostructures by heteroepitaxial growth has attracted considerable attention. Much interest involves the formation and investigation of vertically and laterally coupled QD. Such coupled QD called quantum dot molecules are interesting not only for basic studies, but also as functional units with applications in quantum information processing and computing.

The aim of the present work is to review present and future trends of research on quantum dot nanostructured semiconductors from fundamental issues of synthesis allowing: a) to improve QD homogeneity in size with keeping form and elemental content; b) to control QD density and 3D QD space ordering; c) to lower the defect density. Spontaneous nucleation of nanocrystals at heteroepitaxy of lattice mismatched semiconductors is described by: a) the dispersion in size averaged with 17-20% for (as example) Ge QD in Si; b) the random nanocrystal nucleation and as a result random arrangement in growth plane. The low energy (about 100 eV) pulsed ion-beam action during molecular beam epitaxy was found to improve noticeable QD size dispersion and to increase QD density as compared with common molecular-beam epitaxy. The QD ordering in space was done by epitaxy on ion-beam induced pit-patterned substrates and effect of vertical alignment of nanocrystal nucleation. The epitaxy on pin-patterned surface allows to reduce Ge size dispersion and QD ordering in the plane of growth. 3D QD crystal formation was obtained with vertical alignment of nanocrystal nucleation at multilayer growth of nanostructure. The strain induced epitaxy in heterophase system was studied to clarify the mechanism of QD nucleation and growth.

Other approach to eliminate QD nonuniformity in as grown nanostructure is based on using pulsed laser annealing of QD in order to improve their structural and electrical properties. Pulsed laser annealing was made in QD nanostructures where heteropair materials have taken with higher melting point for crystal matrix as compared with melting point of QD materials. It can be realized for many usually used heteropairs: Si/Ge, GaAs/InAs, GaN/InN, GaP/InP. The melting temperature was found strongly depend on nanocrystal size: melting temperature is increasing as nanocrystal size goes down. The high-melting crystal matrix keep QD crystal structure easier for smaller QD size. It is fundamental background to improve quantum dot size dispersion at laser annealing of QD nanostructures.

Ge QD enclosed in a silicon matrix represent attractive type of the device due to its compatibility with standard Si readout circuitry. Intersubband optical transitions in quantum dots have a great deal of attention due to their potential applications in infrared detectors operating at normal incidence and displaying low dark current. Recently, it was reported on the photovoltaic operation of a p-type ten-period Ge/Si QD infra-red photo detector with Johnson-noise limited detectivity as high as 6.2×10^{10} cm $Hz^{1/2}$/ W at λ=3 µm and at 90 K.

Predictive modeling of self-catalyzed GaAs nanowire growth

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Modeling vapor-solid-liquid (VLS) growth of III-V nanowires (NWs) mediated by a foreign catalyst (such as Au) is made tricky by the complex composition of the droplet and the multiplicity of material pathways involved. Actually, by confronting models and experiments, only a few quantities have been estimated so far (group III diffusion lengths, supersaturation...). Modeling self-catalyzed growth [1] is potentially simpler. In particular, the thermodynamics of the (III,V) liquid that constitutes the droplet are known. Moreover, for GaAs at least, a striking feature of this method is that the NW growth rate is governed by the group V (As) flux supplied to the sample and varies linearly with it [1,2]. At the same time, As surface diffusion is negligible [2].

We have thus developed an 'As-only' fully quantitative model of the self-catalyzed MBE growth of GaAs NWs, that depends on only a few *a priori* unknown physical parameters. The model relies on As material balance between the 3 VLS phases and includes nucleation, evaporation and capture of As re-emitted by the NW environment [2]. It reproduces quantitatively all salient features of our experimental study [2], in particular the variations of NW growth rate with As flux, temperature and NW radius.

From these fits, we extract a complete set of model parameters, in particular the nucleus edge energy. We also determine quantities so far inaccessible to experiment, such as droplet composition (about 1%), liquid supersaturation and nucleation barrier, for individual NWs. The model can then be used to predict the growth rate (and all quantities of interest, such as supersaturation or nucleation barrier) for arbitrary GaAs NWs in arbitrary growth conditions, including conditions not yet explored experimentally. To conclude, although largely ignoring group III elements, our model seems to capture most of the physics of self-catalyzed growth.

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Stopping and resuming at will the Ga-catalyzedgrowth of GaAs nanowires

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In this talk, we will first discuss some general aspects of the Ga-catalyzed synthesis of GaAs nanowires: formation mechanisms, growth on Si substrates and avoidance of polytypism [1,2]. We then demonstrate the possibility of interrupting and resuming at will the self-assisted growth of GaAs nanowires by molecular beam epitaxy[3]. The Ga nanoparticles assisting nanowire growth on Si-treated GaAs(111)B substrates are consumed by exposure to an As flux. Condensation of new Gananoparticle on the top facets of the existing nanowires is achieved by exposing the nanowires to a Ga flux. The new Ga nanoparticles are found to assist the growth of new GaAs nanowires in epitaxial relation with the previous nanowires. The growth and the regrowth processes of the nanowires are both described by an analytical model that is able to reproduce very well the observed experimental time-dependence of nanowire length and diameter during regular growth and regrowth stage. This new mechanism can be used in tailoring the axial and radial nanowire heterostructures sheds more light on the self-catalyzed growth of III-V nanowires in general.

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Semiconductor nanowires for optoelectronics

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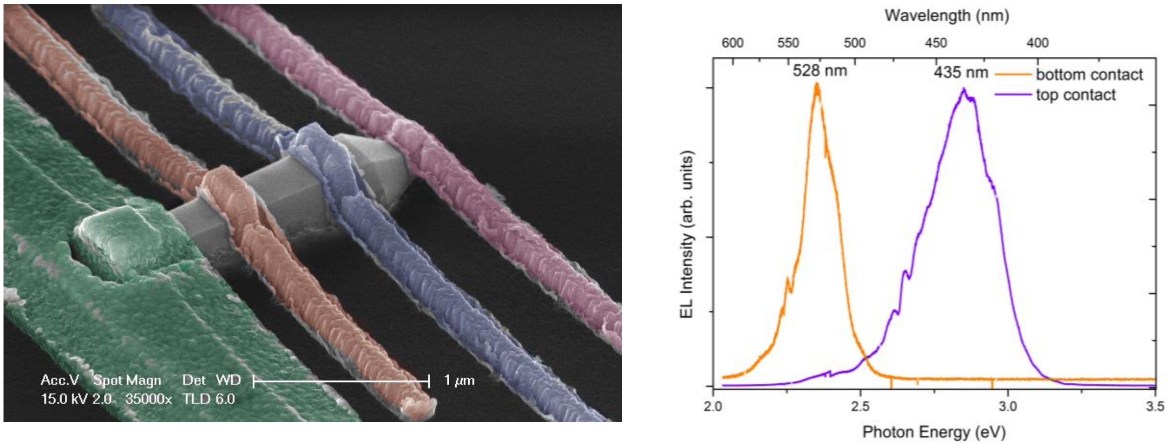
The present need for the miniaturization of electronic and optoelectronic components has motivated the search for new nanoscale functional materials. In this context, semiconductor nanowires are intensively studied as promising building blocks of future integrated photonic and electronic platforms. They are also unique systems to study fundamental physical phenomena at the nanoscale. The nanowires are nano-objects with a high aspect ratio having a diameter spanning from several nanometers to several hundreds of nanometers and a length that can be tuned from hundreds of nanometers up to hundreds of microns. These subwavelength structures exhibit unique optical and electrical properties stemming from their anisotropic geometry, high surface-to-volume ratio, and carrier confinement. The applications of semiconductor nanowires cover the transistors, sensors, power elements as well as optoelectronic components (light emitting diodes, photodetectors and amplifiers).

The nanowires can be fabricated by a bottom-up approach, which provides the possibility to reduce the object dimensions disregarding the limitations imposed by the lithographic techniques while preserving lateral surface flatness. Thanks to the constant effort of the last 20 years, the epitaxial growth techniques have achieved a high degree of control of the composition, doping, and morphology of the nanowires. It is possible to embed axial or radial heterostructures into nanowires to engineer carrier confinement.

In this talk, we will discuss the optical properties of GaN/AlGaN axial and radial nanowire heterostructures in terms of emission energy, polarization and correlation with the nanowire structure. We will then show the potential of these nanostructures for device applications on the example of photodetectors, photovoltaic elements and light emitting diodes.



Figures show a single InGaN/GaN nanowire LED exhibiting either blue or green emission depending on the contact position.

Arsenic pathways in self-catalyzed growth of GaAs nanowires

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Kinetics of III-V nanowire (NW) growth can be explored by varying periodically the incident vapor phase during the elaboration of a ternary compound. Modulations of the NW composition are produced and furnish time markers which indicate precisely how the elongation rate evolves during growth [1].

We use this method ($Al_xGa_{1-x}As$ markers) to investigate the self-catalyzed growth of GaAs NWs by molecular beam epitaxy. We confirm a result previously established [2]: self-catalyzed vapor-liquid-solid growth is driven by the arsenic species. Then, we address the basic question of which pathways are followed by these species. We find that the As flux directly impinging on the catalyst particle is not sufficient to explain the elongation rate. The same conclusion was already derived for the group III atoms. However, while surface diffusion on the NW sidewalls is the main pathway to feed the catalyst with group III atoms [1,3], we exclude this possibility for As_x species. Our experiments indicate that a more realistic source is the re-emission of As_x vapor species from the substrate and NW sidewall surfaces. We estimate this second contribution to be at least as high as the direct flux.

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Optical properties of InAs/InP quantum rod nanowires emitting at telecom wavelengths

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The growth of nanowires (NWs) using Vapor-Liquid-Solid (VLS) method is well adapted to integrate III-V semiconductors on silicon (Si) giving to the NWs technology a great potential in optoelectronics and photonics on Si substrates. At INL, we have investigated the growth of purely wurtzite InAs/InP quantum rod nanowires (QR-NWs) emitting at 1.55 μm on Si(001) and Si(111) substrates by VLS assisted molecular beam epitaxy. The growth procedure has been optimized to avoid the presence of an InAs radial quantum well which is usually formed for such heterostructured NWs grown by VLS-MBE.

The microphotoluminescence study of single QR-NWs at room temperature (RT) reveals linewidths in the 17-22 meV range and a highly linearly polarized emission parallel to the axis of the nanowire. This high degree of linear polarization of emission (> 0.9) and absorption (0.5) can be explained by the photonic nature of the NW structure. At low temperature and low excitation power, single QR-NWs reveal a broad peak with an asymmetric lineshape. From experimental and theoretical studies we conclude that this feature is due to a piezoelectric field induced by the strained wurtzite InAs material.

The high stability of the photoluminescence intensity (the RT integrated photoluminescence intensity is over 30% of the value at 14 K) together with a long lifetime of 7.5 ns at RT confirm a great promise for high efficiency emitters based on InAs/InP QR-NWs grown on silicon substrates.

Photoluminescence studies of InAs/AlAs and GaN/AlN quantum dots

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Semiconductor quantum dots (QDs) are intensively investigated due to their perspective application for novel devices fabrication. Carrier confinement in QDs prevents transition of carriers to nonradiative recombination centers and makes these structures suitable for light-emitting devices.

In present work the atomic structure, energy spectrum and recombination properties of InAs QDs embedded in an AlAs matrix, as well as GaN QDs in an AlN matrix have been investigated.

The InAs/AlAs QDs samples studied in this work were grown by molecular beam epitaxy (MBE) on semi-insulating (001)-oriented GaAs substrates. To fabricate QDs the Stranski-Krastanov growth mode and droplet epitaxy method were used. The structures with GaN/AlN QDs have been grown on sapphire substrates by MBE using ammonia as a nitrogen source. We study the structures grown in the S-K growth mode at relatively high substrate temperature (~900°C) and by kinetically controlled growth without forming a two-dimensional wetting layer, which can be realized at relatively low substrate temperature (~500°C).

The band alignment in the InAs/AlAs QDs is shown to be of type I with the lowest conduction band states at the direct Γ or at the indirect X_{XY} minima of the QD conduction band, depending on the QD's size and composition. The degree of intermixing of InAs and AlAs has been investigated by means of transmission electron microscopy (TEM) and steady-state photoluminescence (PL) compared with theoretical predictions and found to increase with increasing growth temperature and growth interruption. The lifetime of excitons strongly depends on the thickness of the interface diffusion layer, QD_S size, shape, and composition. The different exciton lifetimes, which result in photoluminescence with nonexponential decay obeying a power-law function, can be described by a phenomenological distribution function.

The PL decay law of a GaN/AlN QDs ensemble is also non-exponential in the single-exciton recombination regime. We propose a model explaining the PL kinetics of GaN/AlN QDs ensemble. The model derives the PL decay curves from the QD size distribution measured by TEM. According to the model the GaN/AlN QDs shape fluctuations lead to an essentially non-exponential PL decay law.

Spectroscopy of colloidal semiconductor nanoplatelets

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Physical parameters of semiconductors nanocrystals (NCs) depend of their size, their shape, their surface and their composition. Control of these parameters is important to obtain more efficient NCs for opto-electronic applications. In 2008, our team synthesized the first colloidal NCs with perfect 1D confinement.[1] These NCs have the shape of platelets. These nanoplatelets (NPLs) are atomically flat and have a thickness in the range of 1-2nm. Their laterals dimensions vary from 10nm to almost 1μm.[2,3] NPLs have visible fluorescence and their quantum yield in hexane solution can reach 50%. Such colloidal nanoparticles have electronic properties similar to two dimensional quantum wells and consequently are potential candidates for various quantum devices.[4]

We present nanoplatelets spectroscopy at room and cryogenic temperature. We observe photoluminescence, lifetime intensity decay and fluorescence intensity at different temperatures for both ensemble of nanoplatelets and single nanoplatelets.[4,5] This study shows that NPLs have some optical properties which differ from classical colloidal CdSe NCs. Control of the confinement at the atomic level leads to a perfect monodispersity of some optical properties. At low temperature, the NPLs radiative lifetime of the exciton is 3 orders of magnitude shorter than typical lifetime in colloidal NCs. This makes the nanoplatelets the fastest colloidal fluorescent emitters and confirms that they are the colloidal equivalent of semiconductor quantum wells formed by molecular beam epitaxy. In addition we show that nanoplatelets can self-assemble to form 1D superlattice. When self-assembled, an additional emission line appears in the photoluminescence spectrum at low temperatures.[6] This emission line is a collective effect, not observed when the nanoplatelets are not self-assembled. It is attributed to the longitudinal optical (LO) phonon replica of the band-edge exciton and its presence in self-assembled nanoplatelets only, is explained using a model based on the efficient photons re-absorption between neighboring nanoplatelets.

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Chemical bonding effects in complex oxyfluorides with transition metals

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Complex transition metal oxyfluorides are interesting materials because the drastic distortion of metal-(O,F) polyhedra in a crystal lattice is achievable due to the different ionicity of metal-O and metal-F bonds. The anionic sublattices of these compounds are generally the [$MO_{6-x}F_x$] (M = W, Mo, Nb, Ti; x = 3, 4, 5) octahedral groups. The crystal structure and some physical properties have been reported for several oxyfluoride compounds. However, the accurate investigations on the electronic structure of the oxyfluorides are practically absent mainly due to the lack of high-quality samples.

In the present study, the electronic structure of G2-$K_3WO_3F_3$ and $CsMnMoO_3F_3$, where O/F = 1, and G0-Rb_2KTiOF_5, ratio O/F = 0.2, has been measured with X-ray photoelectron spectroscopy for the first time. The chemical bonding effects, appeared due to the mixed O/F anion system, are explored using core level XPS and compared to those in the previously measured oxides and fluorides. The structural parameters of the oxyfluorides have been refined by Rietveld method at T = 298 K. Electronic structure observation shows interesting chemical bonding effects appeared due to presence of O/F anion complex in the crystal lattice. In the result of a wide comparison of BE values of representative core levels measured by XPS in oxides, fluorides and oxyfluorides containing K^+, Rb^+, Cs^+, Mn^{2+}, Ti^{4+}, Mo^{6+} and W^{6+} cations, it is found that cation-anion bond ionicity is noticeably dependent on the O/F ratio in oxyfluorides. In G0-Rb_2KTiOF_5, the most pronounced effect is detected for Ti-O/F bonding, where bonds are of partly covalent character. In $CsMnMoO_3F_3$ oxyfluoride, similar effects were found for Cs^+, Mn^{2+} and Mo^{6+} ions. Thus, the variation of bond ionicity due to the competition of O^{2-} and F^- ions for the valence electrons provided by metals seems to be a general phenomenon in oxyfluorides. If this is the case, the earlier created systems of effective ionic radii in oxides and fluorides may be not correct in oxyfluorides and the creation of developed radii systems is topical, where the dependence of effective ionic radii on the O/F ratio is accounted for.

The study was partially supported by SB RAS (Grant 28.13).

Tuesday, June 4

Controlled and catalytic fluorination to prepare graphene and fluorinated graphene

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Graphene, an infinite two-dimensional layer consisting of sp^2 hybridized carbon atoms, has been attracting considerable interest in recent years because of its unique band structure and physical properties. The preparation of fluorinated graphene is still a real challenge because of its reactivity with fluorine gas, even diluted with an inert gas (N_2 or Ar). Graphene strongly reacts with molecular fluorine F_2 to form volatile CF_4 and C_2F_6 species. In other terms, graphene burns in fluorine atmosphere. Our strategy consists then to fluorinate graphite flakes and to perform a mechanical exfoliation. Xenon difluoride has been chosen as fluorinating agent (FA). This method results in a homogenous dispersion of fluorine atoms into the whole volume of graphite, contrary to F_2 gas, and favours the mechanical exfoliation by cleavage of the fluorocarbon sheets [1,2].

Fluorination allows also non-fluorinated graphene materials to be synthesized using two strategies:

(i) Using a two-step strategy with controlled fluorination (with solid FA) followed by a thermal defluorination [3]; the synthesis of sub-fluorinated graphitized nanodiscs was first performed. The fluorinated parts must be homogenously dispersed in the carbon lattice with a non-fluorinated core (the process is called sub-fluorination). A controlled fluorination using solid FA (TbF_4) was then preferred rather than the direct process using F_2. Whatever the fluorination method, the removal of the fluorinated parts during a process similar to a peeling with CF_4 and C_2F_6 gas evolution does not result in damages of the non-fluorinated region. Multilayer carbonaceous nanomaterials were synthesized in a form of ruffled paper [4]. The discs fold up on themselves during thinning.

(ii) A chemical exfoliation of graphite fluorides (GFs) prepared at room temperature. Contrary to the conventional method using F_2 at high temperature in the 300-600°C range, the fluorination of graphite can be performed at room temperature thanks to a catalytic gaseous mixture of F_2, HF and iodine pentafluoride IF_5. The resulting room temperature GFs contain intercalated residual catalysts, such as IF_5, IF_6^- and IF_7 and the covalence of the C-F is weakened in comparison with high temperature GFs. In order both to strengthen the C-F bond and to remove the residual catalysts, a post-treatment was carried out. The resulting samples were then exfoliated using a thermal shock. Fast evolution of gaseous iodine species resulted in the exfoliation/defluorination of graphite. The thermal defluorination and the nature of the sheets were investigated by thermogravimetry and electronic microscopies, respectively. Electrochemical discharge in primary lithium battery was also used to check the presence of residual C-F bonds and their covalence. This underlines that non-fluorinated graphene can be obtained by this original way. Finally, the dispersion of those samples was studied in different polar and non-polar solvents; In order to enhance the dispersion, the graphene materials were post-fluorinated.

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Functionalization of few-layer graphene for electronic applications

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Functionalization is very promising approach for creation of new materialы, modification of the material properties and widening of their application spectrum. We consider in the report last our advanced structures created with use of covalent functionalization of few-layer graphene. 2D materials require high quality substrate to provide their functionality. We have suggested new approaches to the solution of this problem. The first approach is based on chemical functionalization of few-layer graphene (intercalation of the widely used organic solvent N-methylpyrrolidone with subsequent annealing in the temperature range of 100 – 170^{o}C) which led to formation of the high resistivity derivative with subsequent cleaning of the surface and recovering of the top layer conductivity. Investigation of properties of the top graphene layer with repairing conductivity demonstrates that it is chemically modified graphene with high conductivity and high carrier mobility (up to 42 000 cm^2/Vs). Moreover, the conductivity of this monolayer is modulated on 3 - 4 orders of magnitude by gate v1oltage. These properties provide the high perspective of this material for electronic applications. The second approach is based on fabrication of an additional organic (1-alcene) monolayer on SiO_2/Si substrate. This layer leads to electrical passivation of the surface and also provides the increase in field-effect carrier mobility. Functionalization of few-layer graphene in allows us to create the system of graphene conductive islands (quantum dots, QDs) with size 50-100 nm or lower in the insulating matrix due to self-organized corrugated process during chemical treatment in an HF aqueous solution. The study of electronic structure of QD system was made by means of charge spectroscopy (Q-DLTS) in combination with temperature (80-300 K) dependence of conductivity. The first results of this study will also discusse in the report.

Examples of optically driven devices based on graphene and carbon nanotubes for solid state and vacuum Nanoelectronics

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We are currently studying two different kinds of optically driven devices. The first one is a solid state device based on a dual gate graphene transistor. To fabricate the device, we have first transferred graphene on a Si n+/SiO_2 substrate acting as a back gate. After patterning the graphene layer, metal contacts have been deposited. Then, we implemented on these transistors a stack comprising a metallic top gate and an Al_2O_3 dielectric film. The transistor characteristics show that the drain current can be effectively controlled with a small voltage applied to the top gate. First electrical measurements of the graphene transistor under laser illumination will be presented.

The second device is a CNT photocathode. This photocathode is an array of vertically aligned multiwalled CNTs (electron emitters), each CNT being associated with a p-i-n photodiode. Compared to conventional photocathodes, the functions of photon-electron conversion and electron emission are separated. This photocathode combines the very good field emission properties of carbon nanotubes and the excellent efficiency provided by semiconductor photodiodes. Using an X-ray tube based on such photocathodes, we will show the optical control of X-ray emission. The application domain concerns stationary scanners for 3D X-ray imaging.

This work has been funded through the EC NMP projects TECHNOTUBES and GRAFOL.

Collaborators: M-B Martin and P. Seneor (CNRS), JP Mazellier, M. Piquemal, L. Gangloff, F. Andrianiazy, S. Maine, S. Xavier, O. Bezencenet, N. Martinez, G. Becker, C. Bourat and P. Ponard (Thales)

Bromination of double-walled carbon nanotubes and perforated graphene

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Bromination of graphitic materials is attractive for development of polar covalent bonds which should result in changes in the electronic properties and reactivity of the material. Here, for bromination we chose two kinds of graphitic materials: double-walled carbon nanotubes (DWCNTs) and perforated graphite. The DWCNTs were produced by catalytic decomposition of CH_4 vapor over $Mg_{1-x}Co_xO$ solid solution containing small additions of molybdenum. The perforated graphite was obtained with boiling the graphite oxide in sulfuric acid. The functionalization of materials was performed by bromine vapor at room temperature during a few days. The products were characterized by high-resolution transmission electron microscopy (HR TEM), Raman scattering, and X-ray photoelectron spectroscopy (XPS). The concentration of bromine in DWCNTs and perforated graphite was estimated from the XPS data to be 5.6 and 8.6 at%, respectively. From the analysis of spectroscopic data, the products contain adsorbed Br_2 molecules and covalently bonded bromine. The first bromine specie prevails in the Br-DWCNTs, while in the perforated graphene the most of bromine is included in the C–Br bonds. Quantum-chemical calculations of interaction of bromine with fragments of a CNT and graphene confirm that Br_2 molecules adsorb on the perfect graphitic surface while they can dissociate near dangling bond defect sites with the formation of covalent C–Br bonds. Thus, any covalent attachment of bromine to the graphitic surface achieved at room temperature is likely related with defects. This conclusion is supported by higher reactivity of perforated graphene with bromine as compare to the DWCNTs, where vacancies could be produced in processes of nanotube growth and purification. The distribution of bromine atoms on a graphene layer was visualized by the HR TEM.

Carbon nanoscrolls production and properties

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Carbon nanoscrolls (CNS), formed by spirally coiled graphene sheets, belong to a family of carbon nanomaterials [1]. The conical CNSs with polygonal cross sections have been produced previously by chemical vapor deposition (CVD) [2]. Here we report results of our recent investigations on synthesis and structural characterization of the CNS. The carbon deposits on Si substrates containing CNS were obtained, using direct current discharge plasma activated CVD system [3]. Carbon-carbon composites containing CNS, graphitic and diamond materials in different proportions were fabricated, using variation of the CVD process parameters. Raman, SEM, HR TEM in combination with FEB was applied to evaluate structural characteristics of the CNS.

The obtained CNSs have conical needle-like shape and are formed by a spirally wrapped single graphene sheets. Most of the CNS needles have shapes of twisted prisms with polygonal cross-sections similar to that reported in [2]. These needles are oriented in the CVD films along a normal. We found that the CNS structures originate from surface of diamond crystallites, which formed during the CVD process. HRTEM investigations demonstrate well-ordered transformation of diamond atomic structure into CNS or graphite. Based on these experimental observations, we propose a model for CNS formation during condensation of carbon atoms from a vapor.

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Applications of the of the dynamic spray-gun deposition method fromSupercapacitor electrode based on mixtures of graphite/graphene and carbon nanotubes to GO, R-GO nonvolatile memories

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Hybrids of carbon nanotubes with nucleic acids fragments as platform for therapeutics and diagnostics

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The recent advances in carbon nanotubes (CNT) synthesis and modification provoked the great progress of their application in the different areas of biology and medicinal chemistry. The employment of CNT as nanocarriers for the therapeutic nucleic acids (NA) as well as new diagnostic tools is very prospective.

A new strategy of design of multifunctional SWCNT hybrids containing fluorescent groups and therapeutic NA (siRNA or antisense oligonucleotides) was developed. We expect these constructs to be low-toxic and effective in interaction with cell membrane and therefore they could be good transporters of therapeutic NA. The physico-chemical properties of these hybrids were investigated. We constructed a new type of the electrochemical biosensor based on hybrid of oligonucleotide with vertically aligned MWCNT as sensitive element and demonstrated its potential for detection of NA.

Hybrid materials containing nucleic acids could be regarded as a basis for the therapeutics and diagnostics in nearest future.

This work was supported by RFBR (projects№12-04-91053-PICS, №- 11-04-01014) and Federal Targeted Program "Scientific and Scientific-Pedagogical Personnel of the Innovative Russia" for 2009-2013 (contracts № 8653 and № 8739).

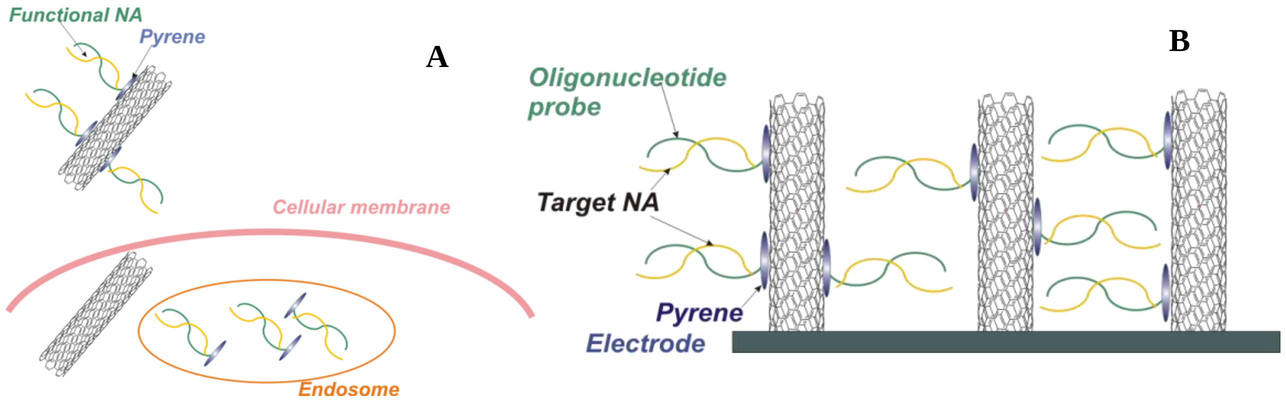

Figure 1. A – Delivery of therapeutic NA (siRNA) by using their hybrids with SWCNT.
B – Electrochemical biosensor based on hybrids of oligonucleotide with MWCNT.

Measurements of electrical and thermal transport in high quality Si nanowires using field emission

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Silicon Nanowires (SiNWs) are being studied for a wide variety of applications with significant progress in their integration into devices such as transistors, solar cells, photodectors, chemical sensors, etc. However there has been much less work on field emission (FE) even though their semiconducting properties open distinct possibilities compared to metallic emitters and carbon nanotubes. We report here on FE studies of individual high crystalline SiNWs with controlled surface passivation [1]. Extensive I-V, FE microscopy and FE energy spectroscopy measurements were performed in an ultra high vacuum system. Quasi-ideal saturation was obtained accompanied by a strong sensitivity to temperature. Using energy spectra of the emitted electrons, a simple p-n junction model taking into account the low dimensionality of the NWs allowed us to estimate the doping and carrier lifetime. The role of the surface states was demonstrated by cyclic heating and hydrogen passivation treatments done *in situ*. This treatment allowed us to determine that the current saturation is linked to the conducting properties of the Si/SiO_2 interface of the NWs. FE Measurements of the thermal response time through modulated laser stimulation and a new negative differential resistance effect will also be presneted.

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Dielectric confinement effects in low-dimensional semiconductor heterostructures

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Strong dielectric confinement effects are predicted for heterostructures exhibiting 2D electronic properties. Self-assembled hybrid organic layered perovskites[1] (SAHOP) grown by spin-coating technique could enable superior optical functions and greatly enhance device performances. CdSe nanoplatelets (NP) are flat nano-objects of a few monolayers-thick semiconductors grown using colloidal methods[2]. SAHOP[3] and NP materials are studied by using a combination of Density Functional Theory[4] (DFT) and empirical methods to analyse the dielectric confinement effect on single particle properties and excitonic binding. The organic layer plays a fundamental role in the dielectric confinement. Moreover, in SAHOP and NP nanostructures, excitons strongly localize in the inorganic layers, thus leading to very large binding energies of few hundreds of meV. This e-h-interaction increase can be described by introduction of virtual “dielectric image” charges that actually account for surface polarization and accompany the real carriers in the semiconductor. Some further refinements are proposed using nanosmoothing of induced local polarization.

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Structure and composition peculiarities of GaN/AlN multiple quantum wells and GeSi quantum rings by EXAFS spectroscopy

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Multiple quantum wells (MQW) are promising materials for novel optical applications. They serve as base materials for light emitting devices operating in ultraviolet spectral region, and high-speed infrared intersubband optical modulators and photodetectors [1]. Hexagonal GaN/AlN MQW with 400 nm thick AlN buffer layer were grown by ammonia MBE on (0001) oriented sapphire substrates. GaN well and AlN barrier thicknesses were varied from 1.0 to 4.0 monolayers, whereas the number of period ranges from 20 to 260. It is well known that the optical properties of nitride QWs are strongly affected by arrangement of heterointerfaces.

The particular nanostructure (quantum ring – QR) is a symmetric assembly of four quantum dots bound by a central pit and has been suggested as a candidate structure for logic architecture based on quantum cellular automata [2]. Ge/Si structures with QRs was grown by molecular beam epitaxy. The array of self-assembled GeSi QDs was formed by the following deposition of Ge on Si(100) substrate at the temperature about 700°C. Then, structure GeSi QRs were created by partially Si capping on QDs. After this, a few monolayers of Ge deposited over QRs. Thus, GeSi QRs were used as strain-patterning template for nucleation of Ge QDs in the next layer.

EXAFS (Extended X-ray Absorption Fine Structure) above the GaK and GeK edge [3,4] have been used to study the local structure of heterointerfaces in Ge/Si and GaN/AlN structures grown by molecular beam epitaxy.

GaN/AlN MQWs. Thickness of AlN and GaN layers in MQWs were evaluated using HRTEM (High-Resolution Transmission Electron Microscopy), X-ray diffraction and Raman-spectroscopy. Two sets of MQWs structures with the number of period about of 20 and more than 100 were studied. The Ga-Ga interatomic distance in MQWs is lower than that in the bulk GaN due to elastic compression of GaN layers in MQWs. This effect is less pronounced in thick structures because of almost full relaxation of GaN layers. The Ga-Al interatomic distance in thick MQWs is too long (about 0.1 Angstrom longer than typical values for AlGaN alloys). The effect may be due to generation of vacancies at the interfaces. Number of Ga cations in second coordination shell of Ga atoms is lower than one predicted for abrupt heterointerfaces that evidences in intermixing of heterointerfaces. An intermixing degree depends on total thickness of MQWs.

Ge/Si QRs. It was found that in the first phase of growth (application of the priming layers Si/Ge at ≈ 700 ° C) Ge atoms concentration is ≈ 25%. With further growth (applying the base layers) Ge concentration increases up to 35-45%, depending on the temperature of deposition (610 - 550 °C). It was established for the samples with gross formula Ge_xSi_{1-x} ($0.25 < x < 0.45$), that interatomic distances Ge-Ge and Ge-Si correspond to distances, defined in [5] for solid solutions and in [4] for quantum dots Ge/Si.

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Characterization of nanoparticles through their low frequency vibrations

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Over the past decade, very low frequency Raman/Brillouin scattering has proved to be a powerful technique to probe nanoparticles (~5-20 nm). When the nanoparticles are metallic (Au [1], AgAu [2] and Cu [3,4]), it is possible to detect very diluted amounts of nanoparticles (< 0.01 volume%) thanks to the coupling between the surface plasmon excitations and the low frequency vibration modes. Semi-conductor nanoparticles can also be efficiently probed through low frequency Raman scattering due to resonant electron-hole excitation.

From recently studied cases, including glass embedded nanoparticles, supercrystals of nanoparticles and anisotropic nanoparticles, we will illustrate the various possibilities offered by the low frequency Raman probe, such as size determination and nanoparticle crystalline quality.

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Electrical spin injection at ferromagnet/oxide/semiconductor interfaces probed by magnetoresistance and spin-pumping experiments

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In the focus of spintronics with semiconductors, a proper electrical spin injection into the conduction band of semiconductors is essential for exploring new functionalities like the electrical manipulation by a gate voltage and electrical detection of a spin current between ferromagnetic source and drain. Among semiconductors, Ge is a material of a great interest for high carrier mobility, long spin diffusion length and large spin-orbit coupling to perform electric field spin manipulation through Rashba interactions. The up-to-date studies in various group IV (Si and Ge) and III-V (GaAs) systems concern the measurement of the spin accumulation created by injecting a current at ferromagnetic/oxide/semiconductor interfaces by a three-point electrical Hanle and inverted Hanle techniques [1-3]. In the main systems investigated worldwide, the strong spin amplification evidenced at a single interface is related to a two-step spin injection process through a band-tail of evanescent electronic states at the specific oxide/semiconductor interface. In my presentation, combining magnetoresistance and spin-pumping experimental techniques, we will show how, and unlike in GaAs systems, an efficient spin injection can be reached in the conduction band of Ge despite the presence of interface states [4-5]. We reveal a clear transition from spin injection into electronic states in GOI at the interface with CoFeB/MgO spin injector [5]. Beyond a spin signal amplification at low temperature, we observe a clear transition to a spin injection in the channel above 200K up to room temperature. In this temperature range, the spin signal is reduced to a value compatible with spin diffusion model. Even more interesting we could demonstrate a direct spin injection in the conduction band in Ge through spin-pumping effects and inverted spin-hall mechanism involving the ferromagnetic resonance of the CoFeB layer [5]. In the end, in a more global approach and unlike in metallic tunnel junctions, I will emphasize on the physics of spin injection into semiconductors by spin pumping effects involving a large band of localized states at the interface with the tunnel barrier and whose presence is necessary to induce spin accumulation in the semiconductor region.

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Poster session

Electronic structure of α-SrB_4O_7: experiment and theory

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The noncentrosymmetric optical borate crystals are the basic materials of modern high-power laser systems because of appropriate nonlinear optical (NLO) coefficients, wide transparency window including visible and UV ranges and high optical damage thresholds. Orthorhombic strontium tetraborate α-SrB_4O_7 (SBO) was discovered in binary system SrO-B_2O_3 many years ago and crystal structure is shown in Fig. 1. Recently it was found that this crystal enables enhanced VUV generation through its transparency window down to 121 nm. Thus, the present study is aimed at a complex evaluation of electronic structure of SBO by X-ray photoelectron spectroscopy (XPS). For this purpose the high-quality SBO crystal shown in Fig. 2 has been grown. For comparison, the SBO band structure calculations are implemented using the DFT approach with an HSE functional. The investigation of valence band structure and electronic parameters of constituent element core levels of α-SrB_4O_7 has been carried out with X-ray photoemission spectroscopy. Optical quality crystal α-SrB_4O_7 has been grown by Czochralski method. Detailed photoemission spectra of the element core levels have been recorded from the powder sample under excitation by nonmonochromatic Al Kα radiation (1486.6 eV). The band structure of α-SrB_4O_7 has been calculated by *ab initio* methods and compared to XPS measurements. It has been found that the band structure of α-SrB_4O_7 is weakly dependent on the Sr-related states.

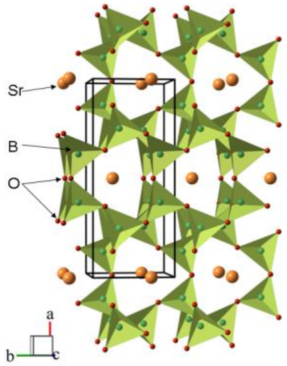

Figure 1. Crystal structure of α-SrB_4O_7.

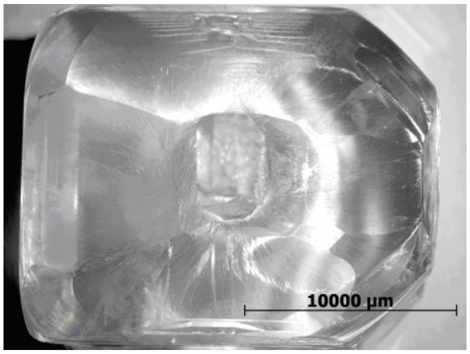

Figure 2. α-SrB_4O_7 crystal grown by the developed Czochralski technique.

Zero-field ^{59}Co NMR for characterization metallic cobalt magnetic nanoparticles embedded into various matrixes

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NMR in magnetics is a powerful tool for probing local magnetic fields distributions on the nuclei. Since the local, or hyperfine, magnetic field depends also on structural features it allows elucidating structural aspects of cobalt nanoparticles inside various matrixes. Owing to magnetic properties differentiation the signals arising from domain walls and domains helps controlling existence of nanoparticles less than 70 nm in size (since 70 nm is critical size of single-domain particles). Various matrixes stabilize different cobalt structures thus it helps attributing cobalt peaks to a particular stacking.

Growth, chromium distribution and electrical properties of GaSe:Cr single crystals

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The layered ε-GaSe crystals are widely used for IR and THz generation via nonlinear frequency conversion due to their high birefringence and high second order nonlinear optical susceptibility. In attempts to improve the weak hardness and fabricability or tune the linear optical parameters, the doping of GaSe into anion or cation sublattices has been actively applied. The doping of nonlinear optical semiconductors with magnetic elements is interesting for many applications in magnetooptics and spintronics. The present study is aimed to grow the optical-quality GaSe:Cr crystals and produce the complex evaluation of microstructural, chemical and electrical properties.

The Cr-doped GaSe crystals have been grown by Bridgman method. The crystal grown from the melt with C_0 = 0.1 mass % is shown in Fig. 1(b). As it is seen, the cleavage plane (001) is roughly parallel to the ampoule axis and the cleaved surface is of optical quality. So, there is no degradation of atomically-flat GaSe(001) cleaved surface due to Cr-doping. The Cr effective segregation coefficient has been estimated as $K_{\mathrm{eff}} = 0.027\pm0.002$ as it is shown in Fig. 2. The upper limit of chromium content achieved in GaSe:Cr crystal is as low as C_s = 0.006 mass% as determined using atomic adsorption spectroscopy (AAS). Optical transparency range and dispersive optical constants of GaSe:Cr are similar to those in pure GaSe as obtained with optical spectrometry and spectroscopic ellipsometry (SE). The GaSe:Cr is a p-type semiconductor with hole concentration $p = 1\times10^{15}$ cm^{-3} and carrier mobility μ = 20-50 cm^{2}V^{-1}s^{-1} at 300 K.

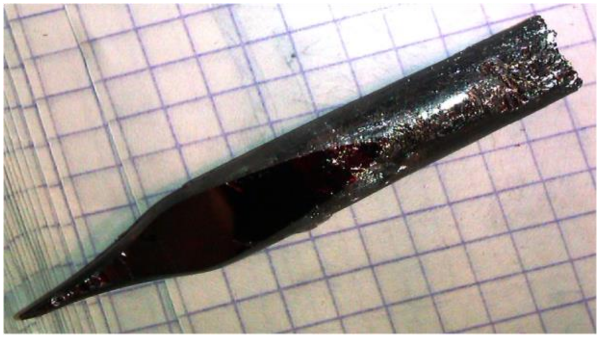

Figure 1. Bridgman grown ingot of GaSe:Cr (0.1 mass % Cr in melt).

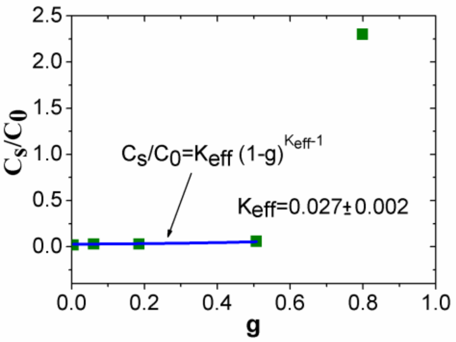

Figure 2. Dependence of real content of Cr in GaSe:Cr (0.1 mass % Cr in melt) on crystallized melt fraction.

Synchronization of two spin transfer vortex oscillators through magnetostatic interaction

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We investigate the synchronization of spin transfer nano-oscillators (STNO) which are interacting through dynamical dipolar coupling. Recently we have demonstrated how magnetostatic interaction influence on phase locking dynamics in a system with two identical STNOs separated by interpillar distance L [1]. Investigating the dynamics in the transient regime toward phase locking, we extract the evolution of the locking time τ, the coupling strength μ, and the interaction energy W.

In this work we have studied synchronization of two vortex STNOs with different frequencies. To realize frequency mismatch, the disks diameters difference $\Delta D/D$ have been introduced. We have provided an analytical description using Thiele approach [2] and have shown that studied system can behave as Adlerian [3] only when $\Delta D/D<5\%$.

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Investigation of multi-wall carbon nanostructures by Raman spectroscopy

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One of the most promising materials for use in various fields of science and technology are carbon nanostructures. Multi-wall carbon nanostructures are very interesting for researchers due to their unique properties, which can be used for a lot of applications. For investigation of various forms of carbon nanostructures (such as single-wall carbon nanotubes, graphene, double-wall carbon nanotubes) a Raman spectroscopy technique has been successfully used. However, for multi-wall carbon nanostructures this method is not yet sufficiently explored. One of the reasons is a difficulty to estimate the exact shells number.

In this work, using the Raman scattering and high-resolution transmission electron microscopy (HRTEM), a comprehensive study of structure of several series of samples of multi-walled carbon nanostructures has been performed. According to HRTEM the quantity of walls, the external sizes and structural features of multi-wall carbon nanostructures of all series was estimated.

In Raman spectroscopy for determination of single-wall carbon nanotubes geometrical parameters the position of the "breathing" mode is used. However in case of multi-wall carbon nanotubes, as a rule, the signal in a low-frequency area is very weak, and can be registered only in resonant conditions. In this regard, it is necessary to investigate other possibilities of Raman spectroscopy for investigation of multi-wall carbon nanotubes. The basic attention has been paid to D (disorder-induced), G (graphite) and 2D (two-phonon scattering)-bands in the Raman spectra. A dependence of the relation of intensities I_{2D}/I_D on the mean diameter of nanotubes and under different temperatures has been detected.

Also the process of thermo-induced transformation of nanodiamonds into carbon onions by Raman spectra has been tracked. The Raman spectra registration has been made in the spectral range 1150 - 2900 cm^{-1}. Each series consisted of the original material and the material subjected to heat treatment at different temperatures. For all sample series the identical dynamics of D- and G-mode shift with the increase of annealing temperature is observed. In some cases, in the high-frequency area the 2D-mode arising has been registered. These changes are explained as a structural change from diamond to graphite (the transition state of sp^3 to sp^2 phase) via formation of onion-like carbon. The thermal threshold of the onion-like carbon formation has been estimated, the dependence of a temperature threshold on the size of initial particles of nanodiamonds has been detected. The results received corresponded well to HRTEM data.

This research was partially supported by the RAS research programs and RFBR 13-02-01354.

Iron(II) spin crossover complexes with hybrid pyrimidine-based ligands: Tuning of ligand field

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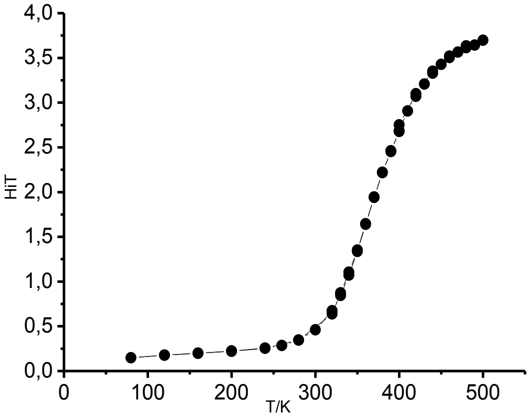
The spin crossover (SCO) in iron(II) complexes has attracted attention due to its fundamental importance and prospects for applications. One of the challenges in this field is the synthesis of complexes undergoing transition at room or higher temperatures.

Iron(II) complexes with 2,6-bis(pyrazolyl)pyridines/pyrazines are one of the flexible groups of SCO compounds [M. A. Halcrow, *Coord. Chem. Rev.* **2009**, *253*, 2493]. We began to study SCO properties of their analogs, *i.e.*, iron(II) complexes with 2,6-bis(1*H*-pyrazol-1-yl)pyrimidines. These ligands appeared to feature rather weak ligand field favoring high spin state either low temperature SCO. To enhance the ligand field and to promote relative stabilization of the low spin state we replaced one of the pyrazol-1-yl groups by the pyridin-2-yl group and synthesized a series of new hybrid ligands, 2-(pyridin-2-yl)-4-(1*H*-pyrazol-1-yl)pyrimidines. First examples of iron(II) complexes with 2-(pyridin-2-yl)-4-(1*H*-pyrazol-1-yl)pyrimidines show high temperature SCO.



The work was financially supported by Russian Foundation for Basic Research (Project 12-03-31032 mol_a).

A comparative study of fluorinated double-walled carbon nanotubes produced by three fluorination techniques

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Fluorination of carbon nanotubes is gateway to modify chemical and physical properties of nanotube surface and wide field of their applications.

In this work fluorination of double-walled carbon nanotubes (DWCNTs) were performed using three different techniques: treatment by F_2 at high temperature, by gaseous BrF_3 at room temperature and by CF_4-plasma treatment. Transmission electron microscopy shows decrease of nanotube rope diameter after fluorination, and the most significant changes are observed in the DWCNTs fluorinated by F_2. X-ray photoelectron spectroscopy reveals that fluorine concentration on surface of the fluorinated DWCNTs depends on fluorination techniques. DWCNTs fluorinated by F_2 have the most fluorine content, while DWCNTs fluorinated by CF_4-plasma have the less fluorination degree. Raman spectroscopy reveals that fluorination induces changes in the vibration structure of DWCNTs. The increasing of intensity of "radial breathing" mode and G-mode of nanotubes is in harmony with fluorination degree of fluorinated DWCNTs. Differences in the electronic structure of fluorinated DWCNTs are observed by near-edge x-ray absorption fine structure spectroscopy (NEXAFS). Comparison of the NEXAFS CK- and FK-edge spectra of fluorinated DWCNTs allows suggesting that local surroundings of CF-groups located on the DWCNT surface are various and depend on the applied fluorination procedure.

In conclusion, the combination of the experimental data shows that DWCNTs fluorinated by F_2, BrF_3 and CF_4-plasma agents have different fluorination degree and distribution of fluorine atoms on the surface of DWCNTs. This suggests that structure and properties of fluorinated nanotubes can be controlled by fluorination technique.

The work was supported by Scholarship of the President of the Russian Federation (СП-1803.2013.1.)

Supercapacitors properties of aligned carbon nanotubes/polyaniline hybrid material

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Electrochemical capacitors, known as supercapacitors, have attracted great interest as promising energy storage devices due to their high power energy density and long cycle performance than conventional dielectric capacitors. Recently, arrays of carbon nanotubes vertically grown on a substrate have attracted attention as a promising material for capacitor electrodes. Carbon nanotubes commonly possess large specific surface area, remarkable chemical inertness and physical stability. Direct contact of carbon nanotubes with conductive substrate provides fast charge/discharge and high stability of capacitor. Here we study effect of orientation and length of carbon nanotubes on the electrochemical performance. Additionally, arrays of aligned carbon nanotubes were used as template for conductive polymer deposition. Among various conductive polymers, polyaniline has emerged as the one of the most promising class of active materials for electrochemical capacitor, due to its high capacitive characteristics, easy processing and environmental friendliness. Formation of three-dimensional conducting network from aligned nanotubes coated with a layer of polyaniline, involved in the Faraday processes, seems to be promising for obtaining of high-performance supercapacitors.

Arrays of vertically aligned carbon nanotubes have been grown on silicon substrates using an aerosol-assistant catalytic chemical vapour deposition (CCVD) method. Toluene was taken as a carbon source, while ferrocene was used as a catalyst source. Solution of 2 wt% ferrocene in toluene was injected during 1 h in CVD reactor heated up to 800 ˚C. The length and defectness of carbon nanotubes were determined by Raman spectroscopy and scanning electron microscopy. Deposition of polyaniline was carried out in two ways. The chemical polycondensation of aniline occurred under an influence of an oxidant in an acidic environment. In our experiments we used sodium persulfate. The electrochemical deposition of polyaniline was performed during the carbon nanotube electrode cycling in a solution of aniline in sulfuric acid in a three-electrode cell with a potentiostat Elins P-30S. Synthesis time was 500-4000 s, the potential range was [-300, 700] mV. Electrochemical measurements showed that the capacity of carbon nanotube electrode increases with the polyaniline coating formation. Furthermore, specific capacity for the composites based on the aligned carbon nanotube arrays is higher than that for the composites from random nanotubes and achieves more than 500 F/g.

Developing of silicon micro- and nanochannel membranes for microfluidic analytical systems

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A versatile technology is presented which enables silicon membranes to be produced over a wide range of channel dimensions from a few nanometres to tens of micrometres. The technology has been realized by two different techniques. In technique referred to as the “top-down” method, a nanochannel part of the membranes is formed by series of CVD operations of Si and SiO_2 directly on a microchannel array, narrowing microchannels from several micrometres to tens of nanometres. In the “bottom-up” method, a porous amorphous silicon film is deposited by CVD on the solid surface of array of microchannels sealed with SiO_2-nanospheres. After removal of silica plugs a porous silicon film 40-400 nm in thick suspended over microchannels is obtained. Pore size in this film can be controllably varied from a few nanometres to tens of nanometres during subsequent processing. The thickness of nano- and microchannel parts of the membranes (length of the channels) is 0.1-6 μm and 100-250 μm, respectively. Surface density of the channels is 10^5-10^8 cm^{-2} and 10^{10}-10^{11} cm^{-2} for the 1-st and the 2-nd methods, respectively.

This method based on quite simple technical processing is competitive with other technologies of fabricating micro- and nanofluidic analytical systems. The structure of obtained membranes comprises a monolithic connection of a nanochannel array with rigid supporting microchannel one and has an ordered open through channels. Coupled with a fluidic system, the device performed in a monocrystalline silicon wafer is intended for transportation, separation, and detection of nanoparticles, cells, polynucleotides and proteins, their conjugates and associates.

This work was supported in part by RFBR grant 12-08-31147 and grant of federal program “Scientific and scientific-pedagogical personnel of innovative Russia” No.8879

Plasma-Enhanced CVD synthesis of carbon composite materials

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Producing of composite materials based on carbon nanotubes (CNT) and diamonds is interest in order to obtain materials those combine unique physical and chemical properties. We analyzed composites derived from CNT arrays on a silicon substrate via depositing sp^3 carbon by means of a microwave PE CVD process.

Arrays of aligned carbon nanotubes have been obtained in a flowing gas-phase chemical reactor, in the thermal decomposition of the reaction mixture at the surface of the silicon substrates area of 10×10 mm^2 the orientation [100]. For the experiment the furnace was heated to a temperature of 800ºC. The flow rate of carrier gas (argon) was 200 ml/min. The reaction mixture, 2% solution of ferrocene ($Fe(C_5H_5)_2$) in toluene ($C_6H_5CH_3$) was fed into the zone of synthesis in the form of an aerosol.

For the formation of the diamond layer and the individual diamond microcrystallites, we used the microwave plasma reactor with an operating frequency amounting to 2.45 GHz and maximum input microwave power of 5 kW at a self-sustaining temperature of the substrate with double-wave pyrometric temperature monitoring. We used a hydrogen-acetone mixture and growth parameters in accordance with the best diamond film quality obtained in preliminary experiments. The hybrid structures obtained were characterized by means of optical and scanning electron microscopy as well as Raman spectroscopy. In most cases, there was a complete burnout of CNTs observed to form a diamond-like component on the substrate surface. Raman spectroscopy characterization and identified an optimal impact time about 6 hours and microwave input power equal to 4 kW. We observed a qualitative evidence for a significant contribution of a diamond-like sp^3 components, whereas the sp^2 component of CNTs was almost undestroyed. According to these data we obtained composite samples on silicon substrates those consist of an array of CNTs and rarely scattered diamond microcrystallites of 1 – 5 µm in size deposited thereon.

Electromagnetic properties of anisotropic composites produced from carbon nanotubes and dielectric polymers

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Anisotropic composite materials, consisting of carbon nanotubes (CNTs) and polymer matrix, are promising materials for electromagnetic (EM) shielding. Here we discuss few methods for development of anisotropic composites. Multiwall CNTs, synthesized by chemical vapor deposition (CVD) method, were used as filler for composite material. Polystyrene was used as a dielectric polymer matrix. In the first way, CNT ordering was achieved by stretching composite materials in the preferred direction. In the second way, anisotropic composite materials were prepared using the forge-rolling method. The forge-rolling method allows to decrease amount of CNT agglomerates and to increase the homogeneity of material. As a result of nanotube reorientation in the polymer matrix during the stretching process, dielectric response of composite materials decreases in comparison with initial value. Angular dependence of the transmitted terahertz radiation was measured for samples, obtained by forge-rolling method, and dielectric response of the composite material was determined in the low frequency region and in the GHz region. Anisotropy of polarized transmitted THz radiation for forge-rolled samples was detected. The dielectric response measurements of anisotropic CNT/polystyrene composites in the low frequency region of two different directions along and across nanotubes in the matrix show increasing of the composite permittivity in the direction of CNT orientation.

Detection of nanoinclusions in the volume of isotropic and anisotropic medium

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Earlier we published the article that runs about the measurements methods of refractive index with the accuracy up to the 7th sign [1]. The zest of the methods consisted in the thing that a flat-parallel plate from an anisotropic plate was used for this purpose, its thickness being determined simultaneously with the accuracy to nm units. In the present report, it runs about the realization of the above-mentioned methods for an isotropic plate. In addition, the limits of the methods and the possibilities of evaluating nanoinclusions in a material's volume are dwelled upon in the present report. Currently, there is no other more precise method to measure flat-parallel plates absolute thickness with the same minimal error. The proofs of the legality of measurement methods for thickness and refractive indexes with such a high accuracy are formulated in this work.

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MoS_2 on aligned CNT arrays: synthesis and electrochemical performance

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Composite materials are widely used for different application. Combination of conducting nanotubes and molybdenum disulfide, which has good lithium intercalation capacity, can produce anode material with high intercalation performance.

MoS_2 particles were synthesized on aligned multiwall nanotubes arrays, produced by CVD method, using ammonia molybdate and thiourea precursors with hydrothermal technique. The samples obtained were studied using scanning electron microscopy with elemental mapping and Raman spectroscopy. Electrochemical performance of the freestanding samples in Li intercalation process was examined in galvanostatic regime. The capacity depends on molybdenum disulfide content. Cycling during 100 cycles reveals material degradation and capacity decrease.

Chemical vapor deposition of graphene on copper

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There are several methods for obtaining graphene. They could be divided into three main groups: mechanical exfoliation, wet chemical methods, chemical vapor deposition (CVD).

In this work CVD method was used for synthesis of graphene. The aim of the work was to obtain samples of graphene for their further functionalization with hydrogen and nitrogen.

Synthesis of graphene was carried out in thermal reactor under ambient pressure. Methane was used as a precursor gas. Copper foil was used as a substrate. Experiments were carried out at different temperatures (970-1010 ^{o}C), varying consists of gas mixtures ($Ar/He+H_2+CH_4$), different exposition times and different rates of samples cooling. Synthesized films were analyzed by Raman-spectroscopy method.

In our experiments were obtained samples of few-layered graphene. Raman-spectra of films synthesized in different conditions were analyzed. It showed that the parameters of cooling significantly affect the properties of films.

Quantum theory of magnetoelectric effect in rare-ears multiferroics

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A quantum theory of magnetoelectric effect in rare-earth multiferroics has been developed on the basis of quantum mechanical approach advanced in [1]. It has been demonstrated here on terbium and holmium alumoborates. This theory leads to the following expressions for the Hamiltonian of magnetoelectric interaction:

$$H_{me} = -ED = -\left(E_+ D_- + E_- D_+ + E_z D_z\right)$$

$$D_\pm = \frac{(D_x \pm D_y)}{\sqrt{2}} = \sum_{p=2,4,6} b_2^p C_{\mp 2}^p + \sum_{p=2,4,6} b_4^p C_{\mp 4}^p$$

$$D_z = b_3^4\left(C_3^4 - C_{-3}^4\right) + b_3^6\left(C_3^6 - C_{-3}^6\right),$$

where b_q^p are constants, $E_{\pm,z}$ are components of electric field and C_k^q are irreducible tensor operators. Dependencies of magnetization, magnetic susceptibility and electric polarization (see fig.) of $TbAl_3(BO_3)_4$ and $HoAl_3(BO_3)_4$ on magnitude and direction of external field and temperature have been calculated in this work with employment of crystal field parameters. A comparison of theoretical results with the experimental data given in [2,3] have been performed, a good agreement has been demonstrated.

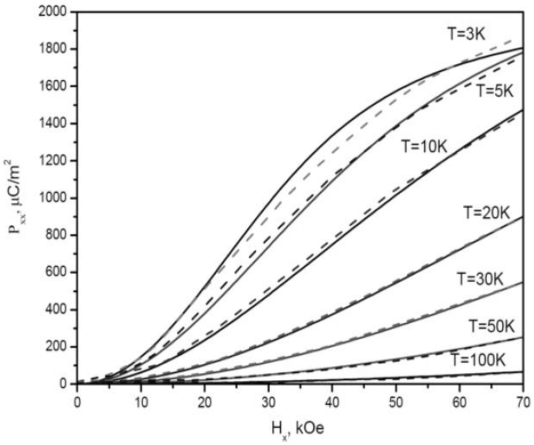

Figure 1. Dependency of polarization in $HoAl_3(BO_3)_4$ on H_X at different temperatures. Dotted curves are the experiment.

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Basal deposition of the carbon flakes on MWCNT surface

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Catalytic CVD MWCNT properties significantly depend on the presence of surface impurities and defects. Amorphous carbon and defective graphene flakes are most common MWCNT surface impurities. In this paper we have investigated the kinetics of carbon species deposition on MWCNT surface during the ethylene decomposition at mild CVD temperatures (600-750°C). The rate reaction equation was derived from kinetic study. Possible reaction pathway based on the kinetic study is also discussed. Carbon-carbon composites produced have been studied with the complex of physical methods such as HRTEM, Raman spectroscopy, synchrotron radiation XRD, DTA, Temperature dependence conductivity and BET surface area to characterize their properties as a function of time, gas feedstock and temperature of the process. The data obtained allows us to discuss this composite as MWCNTs with functionalized surface structure. In addition, it has been shown that we can tune a number of the MWCNT properties (e.g. defect density, outer diameter distribution, observed density of MWCNT, conductivity, BET surface area etc.) by this treatment. These results are important for the optimization of operation parameters of catalytic reactors for the production high quality MWNT (especially in fluidized bed CVD).

Spatial ordering of self-assembled SiGe nanocrystals at heteroepitaxy on strain-patterned substrate

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Nucleation and growth of strained nanocrystals during heteroepitaxy has attracted much interest because of their applications as quantum dots (QDs) in the next-generation electronic and optoelectronic devices. Due to stochastic growth, the size uniformity and spatial order of QDs required for many technological applications are not readily achievable.

In this work the nanostructures with SiGe quantum rings (QRs) served as embedded sources of deformation were used to arrange preferential sites on the growing surface for nucleation of SiGe nanocystals. The implementation of this approach allowed to obtain circular-like configurations of closely spaced QDs (fig.1). It was revealed that the nanocrystals in groups are hut-clusters, which are elongated in [010]-[100] directions and arranged along perimeter of embedded SiGe QRs. The calculations of surface strain energy distribution demonstrated that the preferred orientation of closely spaced QDs triggered by the strain energy anisotropy. The shape and size distributions of spatial ordered SiGe nanocrystals were investigated by atomic force microscopy and scanning tunneling microscopy. The Ge content of grown nanostructures was defined by Raman spectroscopy method. The obtained geometry and composition data were used to calculate energy spectrum of charge carriers localized in QDs by 6-band kp method. These QDs were placed on SiGe QRs embedded in the Si matrix. It was found that the calculated values are in good agreement with results of photoluminescence measurements.

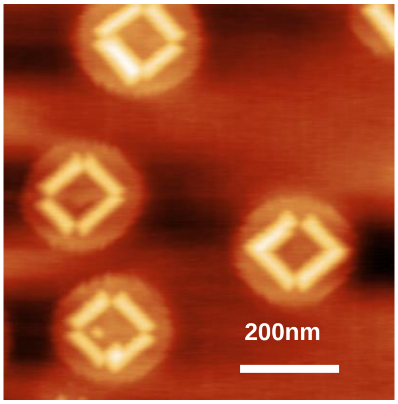

Figure 1. AFM-images of spatial ordered nanocrystals placed on SiGe quantum rings.

This work was supported in part by RFBR (grants 12-02-31077, 12-02-90036).

Non-radiative energy transfer in quantum dot ensemble mediated by localized surface plasmons

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Efficiency increase and control of optical properties of quantum emitters is a challenge in modern nanotechnology. Quantum dots (QDs) have received much attention because they are key elements for diverse advanced devices such as single photon source etc. An efficient approach is to use metal nanoparticles as nanoantennas for QDs. Localized surface plasmons enhance electrical field near the particle thus increasing the efficiency of the emitter.

To realize the coupling we propose to use the ensemble of metal droplets being the initial stage of the droplet epitaxy. It is well known that QDs layers grown close enough tend to align vertically and form stacks due to the distribution of elastic tension in the matrix. The substitution of an upper layer of QDs with droplets should lead to the same self-alignment i.e. the formation of a droplet just over a QD.

To investigate the interaction of plasmons in the droplet and excitons of QDs we grew a structure containing a layer of InAs/AlGaAs QDs with indium droplets on top. According to AFM data under each droplet around 10 QDs are located. Pl spectrum contains a wide peak at 1040 nm corresponding to QDs accompanying by an additional narrow one with the maximum at 1170 nm. We treat the origin of this peak as the resonant interaction of QD excitons with the plasmon mode of the droplet. A long-wavelength part of the wide size distribution of QDs that located under the droplets is in resonance with the surface plasmons in droplets. Due to Purcell effect the spontaneous recombination rate increases. Via plasmon-mediated mechanism the excitation can be efficiently transmitted nonradiatively from QDs surrounding to the QD with the lowest radiative life time resulting in PL enhancement.

The work was supported by RFBR (grant 12-07-31133).

Synthesis, structural and photoluminescence properties of $Ca_2Al_3O_6F:Eu^{2+}$ phosphor

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The incorporation of the halogen ions into oxide crystal lattice leads to a competition between anions for the valence electrons of metal ions. This results in distortion of the coordination polyhedrons, anion disordering and sequent phase transitions on temperature variation, bond ionicity variation and other effects common in oxyhalogenides. Due to these effects, oxyhalogenides possess prononced ability for generation of noncentrosymmetric structures, accommodation of doping elements, specific electronic structure and unusual spectroscopic properties that gives a potential for the creation of new technologically important functional materials with ferroelectric, luminescent, electrochemical and nonlinear optical properties

The $Ca_2Al_3O_6F$ oxyfluoride was recently proposed as an efficient host for the luminescence materials; however the crystal structure remains to be unknown. We present a combined structural analysis on the powder sample of $Ca_2Al_3O_6F$ using X-ray diffraction (XRD), Raman and Infrared spectroscopy technique. XRD studies showed that the structure of crystallized in the rhombohedral system, $R\overline{3}$ space group. The crystal structure consists of almost ideal AlO_4 tetrahedrons, linked through corners, Ca ions in voids, and F disordered to 18 sites around Ca2 ion. Calculated Raman and infrared phonon modes agree qualitatively well with the experimental data. Lattice dynamics simulation based on the simplified version of the Born-Karman potential model. Calculations shows that line at 539cm^{-1}(A_g) corresponds to vibrational mode of six-membered [AlO_4] tetrahedrons ring, and line at 573 cm^{-1}(A_g) corresponds to the full symmetric vibration of fluorine atoms on *ab* crystal plane.

The most interesting result is about the photoluminescence property of Eu^{2+} doped $Ca_2Al_3O_6F$ oxyfluoride. It is known that Eu^{2+} will enter the sites of Ca^{2+}. $Ca_2Al_3O_6F:Eu^{2+}$ shows strong and broad absorption in the near UV regions (260–420 nm) and gives bright green emission peaking at around 502 nm under excitation at 400 nm. The relationship between the crystal structure of $Ca_2Al_3O_6F$ and photoluminescence properties of Eu^{2+} in this host has been evaluated.

The study was partially supported by SB RAS (Grant 28.13).

Creation of a mode-locked microlaser based on photonic crystal and graphene

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Photonic crystal (PhC) is a combination of periodic refractive indices on nanosize scale. It generally exhibits photonic band gaps. Exploiting this property it is possible to make a resonant cavity by constructing a defect in the structure. Having a resonant cavity one can create a continuous wave microlaser by adding an active medium into the PhC slab [1]. Furthermore by applying the saturable absorber one can investigate integrated pulsed microlasers, which is a target of our research. Graphene, a two-dimensional derivative of carbon, possesses such properties [2]. It has unique linear and non-linear optical properties and has already been applied in fiber optics for self mode-locking regimes. In this work we describe the design, fabrication and optical characterization of III–V based photonic crystal microcavities with and without graphene transferred on it.

The construction of our 2D PhCs was performed by electron beam lithography and reactive ion etching technics [3]. The resulting structure consisted of a triangular array of circular air holes in the membrane. Various structures with different parameters were made in order to optimize the coupling between the active medium and the cavity resonances. We used InGaAs/InP quantum wells (QWs) as an active medium emitting around 1.5 um. To characterize our device we performed micro-PL measurements by active medium excitation with pump laser emitting at 805 nm. The sample shows lasing in the range from about 1480 nm to 1590 nm for different structures.

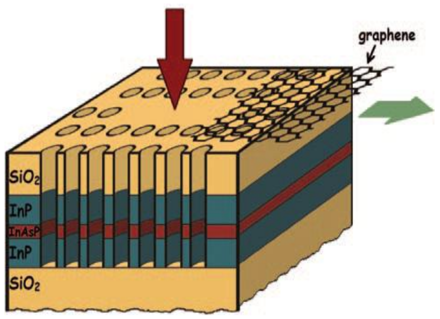

Figure 1. Schematic cross-section view of the PhC micro-cavity integrating a graphene layer on top.

In order to elicit the graphene influence on PL properties of PhC the carbon material was transferred onto PhC surface. Subsequent measurements were performed. These comparative experiments showed the difference in intensity, wavelength and FWHM of resonant cavity peaks.

By optimizing PhC design and experiment conditions we expect to use graphene as a saturable absorber to obtain a train of short optical pulses.

The work was partially supported by RFBR grant 13-02-01354 and French Embassy in Russia.

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Study of morphology, magnetic properties, and visible magnetic circular dichroism of Ni nanoparticles synthesized in SiO_2 by ion implantation

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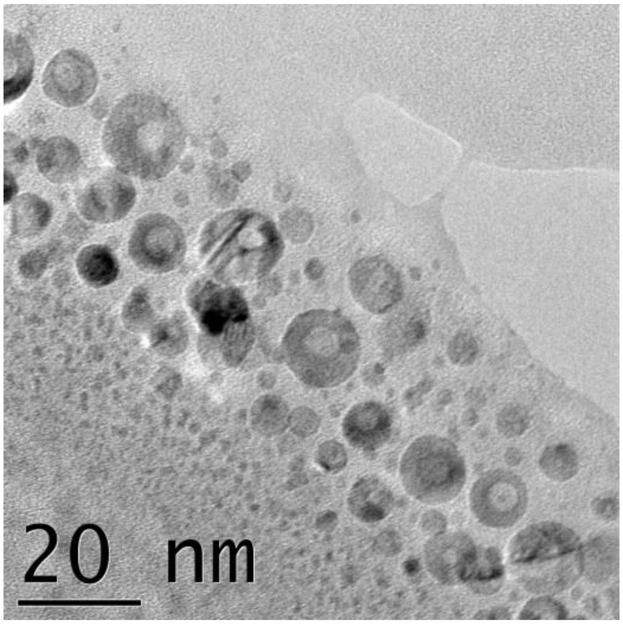
Nickel nanoparticles were fabricated by Ni^+-ion implantation at adose of $(0.5 - 1.0) \times 10^{17}$ ions/cm^2 in a thin near-surface layer of an amorphous SiO_2. TEM characterization of Ni nanoparticles proves the formation of isolatedspherical nickel nanoparticles with the diameters from 2 to 16 nm. The crystal structure and latticeconstant of the nanoparticles corresponds to face-centered cubic Ni. The core-shell nanoparticles in the investigated sample co-exist withordinary pure Ni nanoparticles, what strongly affects the magnetic and especially magneto-opticproperties of the samples. For all three doses, the nanoparticles are in the superparamagneticstate at room temperature passing to the “frozen” state at lower temperatures. TheNi nanoparticles anisotropy constant estimated with the help of ZFC curves appears to exceed thebulk Ni anisotropy second constant approximately by two orders of magnitude. In the spectral range 1.1−4.2 eV the magnetic circulardichroism(MCD) spectrum consistsof two broad maxima of the opposite sign with the characteristics depending on the implantationdose and the measurement temperature. The MCD spectra analysis allows one to show that thehigher energy maximum is related to the surface plasmonresonance (SPR) excitation in pure Ni nanoparticles while lower energy maximum should be associated with the SPR excitation in core-shell nanoparticles.



Nanowires as an effective tool of studying nonequilibrium currents of magnetization in two-dimensional electron system in quantum Hall effect regime

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A two-dimensional electron gas (2DEG) in the quantum Hall effect regime (QHE) demonstrates a hysteresis of magnetization [1], caused by giant nonequilibrium currents of magnetization, induced by magnetic field sweep. We placed a narrow conducting wire in a 2DEG bath to bring two counter propagating nonequilibrium magnetization currents to interaction and found the giant hysteresis of magnetoresistance. Setting the width of the wire one can investigate the spatial distribution of nonequilibrium magnetization currents in conventional magnetoresistance measurements. The dependence of magnetoresistance hysteresis on the wire width has been experimentally studied. The dependence contains the threshold value of width that enables to determine the width of the region occupied by nonequilibrium magnetization currents.

Wires have been fabricated by the electron-beam lithography on the GaAs/AlGaAs heterostructure and demonstrated QHE in high magnetic field. The pronounced hysteresis of magnetoresistance is observed at Hall plateaus corresponding to integer filling factors $\nu = 1$, 2 and 4 of a 2DEG. It is shown that the hysteresis loop area decreases linearly with the wire width vanishing at critical width $W_0 \sim 1.35$ μm. Taking into account the depletion width we can conclude that the nonequilibrium magnetization currents are induced in a narrow region of ~ 0.5 μm wide along the edge. To explain the obtained results we propose a qualitative model of the magnetoresistance hysteresis also explaining the magnetization hysteresis.

The work is supported by RFBR (grant №12-02-00532), Program of DNIT RAS (project №1.13), Program of Presidium of RAS (grant №24.19).

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The density of electronic states in graphene with impurities and structural disorder

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The study of the electron density of states (DOS) in graphene is necessary to understand the processes of electron transport in these materials. DOS in graphene can be influenced by various factors such as temperature, concentration of impurities, structural defects, etc.

We have obtained expression for the contribution to DOS with the help of the method of the temperature Green functions. Multiple elastic electron scattering by impurities and structural inhomogeneities in graphene on a substrate, has been taken into account.

The resulting expression for the contribution to DOS depends on temperature, concentration of impurities and the type of short-range order (determined by the parameter $\sum_i \alpha_i$), and its analysis leads to the following conclusions:

1. Gas adsorption by graphene leads to appearance of a gap in the DOS at the Fermi level, which can be explained by the negative contribution to DOS from multiple elastic electron scattering on structural inhomogeneities. This contribution is negative when $\sum_i \alpha_i < 0$. This result is consistent with the experimental data.

2. Change of defect structure of graphene leads to its metallization, when contribution to DOS at the Fermi level increases. This takes place when $\sum_i \alpha_i < 0$.

3. As the temperature increases the value of $\Delta\nu(\varepsilon_F)$ increases in graphene without impurities (the case of metallization) and it decreases in graphene, saturated gas. This result is supported by experimental data.

3D Monte Carlo Simulation of strained heteroepitaxial growth of Ge on Si (100)

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An efficient method for the 3-dimensional simulation of strained heteroepitaxial growth using kinetic Monte Carlo is presented. The model is based on diamond-like lattice. The surface evolution is simulated as random events of deposition and surface diffusion of adatoms. The actvation energy depends on the number of 1st and 2nd neighbours of adatom and on elastic energy. The elastic energy is calculated using the Keating potential. The endurable speed of computer calculations was achieved by allowing atoms to fluctuate around their equilibrium positions and rejection of minimizing the total energy of the whole system. It was shown that the model reproduces such effects during heteroepitaxial growth Ge on Si(100) as Stranski-Krastanov growth mode (see fig.1) and spatial ordering of nanoclusters in multilayer systems.

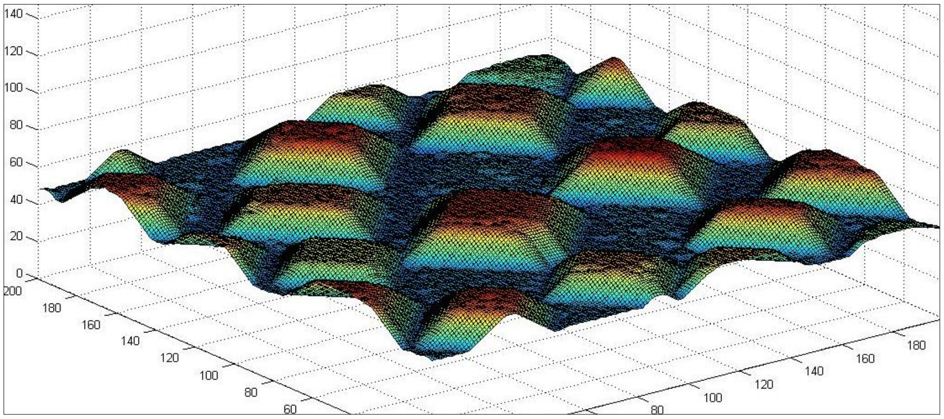

Figure 1. The result of simulation on 25x25 nm substrate.

This work was supported in part by RFBR (grants 13-02-01181, 12-02-31077) and by Program "Scientific and educational personnel of innovation Russia" (grant 8228).

Mechanical stresses and Euler buckling instability in nanoelectromechanical systems fabricated on the basis of GaAs/AlGaAs heterostructures

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The role of mechanical stresses in the fabrication of nanoelectromechanical systems on the basis of GaAs/AlGaAs heterostructures is investigated on the example of suspended nanowires. Despite the lattice mismatch in these heterostructures is vanishingly small the nanowires are subject to Euler buckling instability. The instability effect is found to be enhanced in such systems due to the fabrication process features. Preliminary results show that the nanowires being used as mechanical resonators demonstrate significant softening nonlinearity. The observed peculiarities should be taken into account in the fabrication of nanomechanical and nanoelectromechanical systems [1, 2].

This research has been supported by RFBR Grant Nos. 12-02-31149_mol_a and 12-02-00532.

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Synthesis of carbon nanotubes using polyoxometalates as catalyst precursor

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It is common practice to synthesize of carbon nanotubes (CNTs) by catalytic chemical vapor deposition (CCVD) with the use of inorganic salts of transition metal as a precursor catalyst. More advanced catalysts for commercialized CNT production are still needed. Meanwhile, combination of different metals should ensure progress in an improvement of growing CNTs. Among those the cluster molecules with constant composition promise the best reproductivity of the CNT properties. Supporting it on MgO powder allows us to reduce catalyst particles sintering and increase nanotube yield.

Catalyst is cluster molecules which are attached on the MgO surface by impregnation. Catalyst calcination is carried out in air at 700°C followed by a reduction step in 10 min. Growth of CNT is performed at 900°C from ethylene. As a result black light material which is greater than the initial volume is obtained. Combination Fe-Mo (1:2.5 at.%), Ni-Mo (1:3 at.%), Co-Mo (1:3 at.%) was investigated. Carbon material is characterized using both microscopy and spectroscopy.

Structure, diameter distribution and high performance of the carbon material is shown its usefulness and perspective.

Polyethylene based composites produced by using produced by using pre-adsorbed catalyst on the surface of carbon nanotubes

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Incorporation of multi-wall carbon nanotubes (MWNTs) into the polymer matrix results in significant improvement of polymer properties due to their extraordinary mechanical and electrical properties. In the present work we have investigated the influence of the MWNTs pre-treatment conditions on the catalytically active component adsorption and uniformity of MWNT distribution in the polyethylene matrix (PE) for the preparation of MWNT/PE composites by in situ polymerization method. MWNTs both as synthesized and after oxidation pre-treatment were used. For investigation of the structure of MWNT/PE composites, TEM, SEM, DSC were used. We have found that the controlled oxidation treatment of MWNTs increases the adsorbing ability of TIBA-$TiCl_4$ polymerization catalyst system with the much higher catalytic activity, producing the required amount of PE in the shorter time. It provides homogeneous distribution of catalyst particles along the nanotubes and finally homogeneous coverage of nanotubes surface with PE. For the first time we have observed the Ti-containing catalyst species of the size 2-3 nm on the MWNT surface, stabilized in polymer matrix. The results suggest promising directions for composite MWNT/PE preparation via the catalyst distribution on the surface of MWNTs followed by polymerization of ethylene. MWNT/PE composites with high concentration of homogeneously distributed nanotubes are perspective as polymer carbon nanotubes conductive master batches.

Nonlinear dynamics of bistable spin-valve element

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The universal logic that operates at low switching energy was proposed recently [1]. Information is stored in the position of a single domain wall in a thin, short ferromagnetic wire. The gate is switched by current-driven domain wall motion, and information is read out using a magnetic tunnel junction. All these results were obtained in case of current-in-plane (CIP) geometry. Meanwhile, high efficiency of vertical-current injection for domain wall motion was demonstrated theoretically [2] and experimentally [3]. These results allow us to expect a high efficiency of magnetic domain wall logic in CPP (current perpendicular to the plane) geometry.

Bistable spin-valve element was considered. We present micromagnetic modeling result s of non-local interaction between the current flowing through this element (CPP geometry) and the domain wall. All simulations performed by the finite-difference micromagnetic code, based on the forth-order Runge-Kutta method. The existence of a threshold switching current was demonstrated. It provides the possibility to create a logical “AND” element, based on investigated element. We obtained switching frequency of spin-valve element depending on current density and switching time depending on position of input contact. Also, we demonstrated that even in case, when the input contact is not situated directly above the center of the domain wall, electric current influences sufficient to move DW. The simulations show that the perspective magnetic logic demonstrates characteristics at least not worse than CMOS transistors logic.

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Growth and microstructure of layered centaur crystal GaSe:InS

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The ε-polytype GaSe shows nearly zero hardness by Mohs scale and excellent cleavage properties. As it was shown by AFM observation, the cleaved GaSe(001) surface is almost entirely atomically flat. The hardness increase in GaSe can be achieved by doping. Many single-element dopants have been tested for incorporation into cation or anion sublattices of the GaSe crystal, and the solubility limits and real defect structure were estimated for several solid solutions. The present study is aimed at the crystal growth and complex evaluation of microstructural properties of $(GaSe)_{1-x}(InS)_x$ crystals. The optical quality GaSe:InS single crystal has been grown by modified Bridgman technique using nonstationary temperature distribution for effective melt mixing. The phase composition of the crystal has been verified with XRD and TEM. The chemical composition variation along the crystal has been evaluated with electron probe microanalysis (EPMA), atomic-emission spectrometry with inductively coupled plasma (ICP-AES) and atomic-absorption spectrometry (AAS). The joint solubility limits in GaSe:InS system are measured as y_{In} = 0.28 at% and y_S = 7 at%. The optical properties of GaSe:InS crystal have been obtained with spectroscopic ellipsometry (SE).

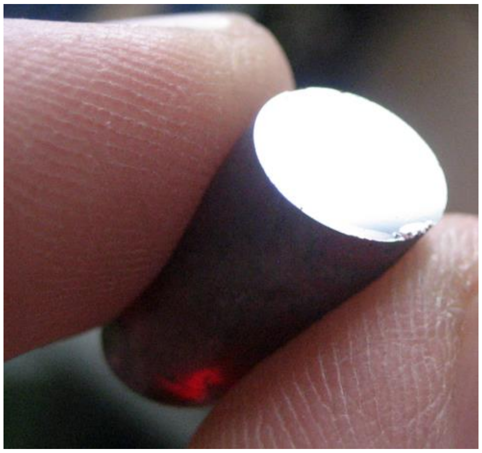

Figure 1. GaSe:InS single crystal illuminated by day sunlight.

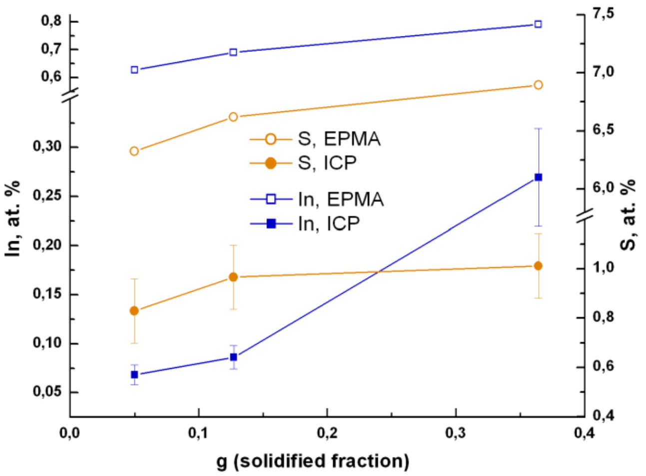

Figure 2. Distribution of S and In over the GaSe:InS crystal.

This study was partly supported by SB RAS under Project 46.13.

Electron localization in multilayer structures with quantum dots

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This work presents the results of the study of electron localization in multilayer structures with different distances between the quantum dots (QD) layers by ESR. Structures with double layers of Ge/Si QDs with Si spacer width *d*=2 nm, *d*=3 nm, *d*=4 nm were grown on Si(100) by molecular beam epitaxy. It turned out that the structure with *d*=2nm is optimal for the localization of the electrons in Δ^{100} and $\Delta^{\bar{1}00}$ valleys near the base edges of QDs. New ESR signal with an axially symmetric g-factor ($g_{||}$=1.9984, $g_{\perp}$=1.9989) was detected. In the structure with *d*=3 nm the ESR signal consists of two overlapping ESR lines with g=2.0004 и g=1.9994. The first signal was related to electrons localized near the outer boundary of the double QD layer, the second signal we refer to electrons localized inside the double layer near the tops of QDs. In the structure with *d*=4 nm the ESR signal from the QD layer is a single line with a nearly isotopic g-factor g=1.9992. This signal is attributed to electrons localized in the Si layer inside the double layer of QDs. The width of the ESR line was changed from ΔH=1.6 Oe to ΔH=2.1 Oe in the structure with *d*=2 nm upon application of light (Fig.1). This broadening of the ESR line is attributed to electron – hole exchange interaction. Estimates of the exchange interaction on the basis of the experimental broadening give the value J=0,1μeV.

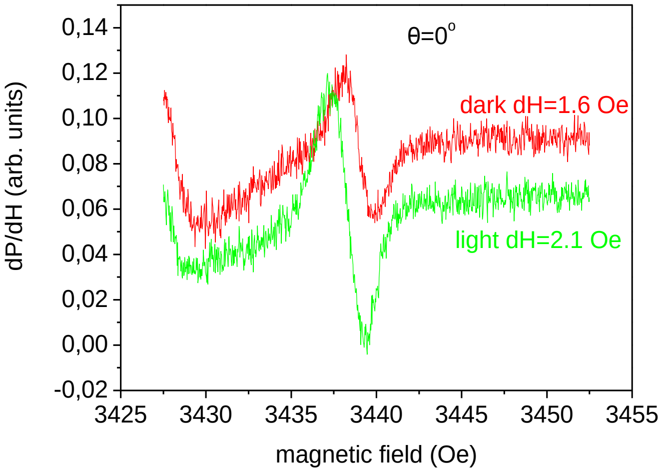

Figure 1. ESR-spectrum of electrons localized in the structures with double Ge/Si QDs, the distance between QD layers d=2 nm. Magnetic field is directed along growth direction of nanostructure (θ=0°).

This work was supported by RFBR (Grant 11-02-00629), by Program of Nanotechnology Department of Russian Academy of Science, SB RAS integration project No. 83, and DNIT project No. 2.5.

Influence of parameters of synthesis on the structure and electrochemical properties of the reduced graphite oxide

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Currently a large number of works devoted to the synthesis of materials based on chemically modified graphene. The wide interest is the chemical properties of graphite oxide. Particularly well studied process of its reduction, leading to the obtaining of structures that contain layers of modified with various oxygen-containing groups graphene. Graphite oxide is relatively easy to obtain, it is dissolved in water and organic solvents. These data formed the basis for the work in which the reduced graphite oxide (rGO) was investigated as a possible material for supercapasitors. However, it was recently shown that various methods and conditions of graphite oxide reduction lead to the formation of materials with different functional composition and electrochemical properties.

We have previously proposed a method for reduction of graphite oxide with using concentrated sulfuric and phosphoric acids [1, 2]. It was found that the functional composition of the product depends on the acid used; however, a systematic study of the influence of synthesis parameters wasn’t carried out.

In the this work, we studied the influence of variation of temperature and time of reduction of graphite oxide in sulfuric acid, phosphoric acid, as well as mixture of these acids on the structure and electrochemical properties of the resulting product. The obtained samples of rGO were investigated by IR and Raman spectroscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. The electrochemical properties of rGO were investigated by cyclic voltammetry.

Based on collected data the dependence of functional composition and supercapacitor properties of rGO from temperature and time of reduction of graphite oxide as well as the type of acid used were determined.

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Synthesis of oriented arrays of silica nanowire bunches by gas-jet electron beam plasma CVD method

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Oriented arrays of silica nanowires were synthesized from mixture monosilane with hydrogen by gas-jet electron beam plasma CVD method for the first time. The synthesis was carried out on silicon substrate with nanometer-sized particles of Sn catalyst. Every particle of catalyst produces bunch of silica nanowires with diameter about 10 nm.

Probably vapor-liquid-solid growth mode was the catalyst-on-bottom (COB) VLS mode, where multiple nanowires grow simultaneously from the surface of one catalyst drop. These silica nanowires were produced at low temperature about 400 °C and with growth rate about 1.6 microns per minute. Growth mechanisms are proposed to explain the results.

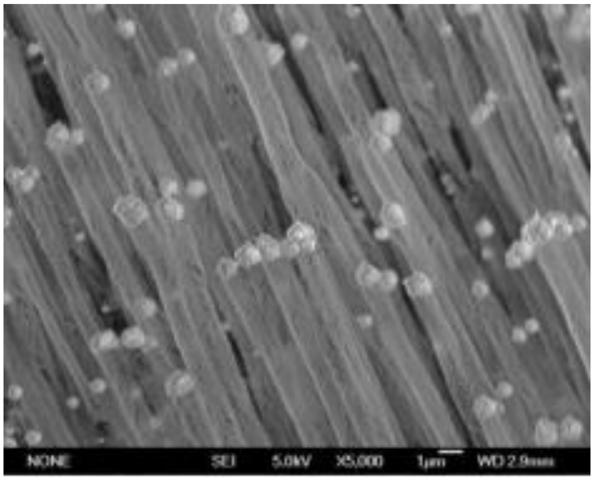

Figure 1. Sn catalyst particles were formed by annealing the substrate in the deposition chamber at a temperature of 400°C under vacuum for 10 min.

Nanostructured suspended semiconductor membranes with two-dimensional electron gas

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Recently there has been growing interest in micro- and nanoelectromechanical systems. Suspended conducting membranes detached from the substrate are one of the examples of such systems. The study of structured semiconductor membranes containing a two-dimensional electron gas (2DEG) gives rise to a number of new interesting phenomena. In the present work we investigate the influence of the heat transport peculiarities on the electron transport in suspended semiconductor membranes nanostructured with square periodical lattice of artificial scatters – antidots.

The membranes were fabricated from AlAs/GaAs heterostructures containing a high mobility 2DEG. Heterostructures were grown above the 400nm thick AlAs sacrificial layer. After the lateral structuring lithography the sacrificial layer was removed by means of selective wet etching.

We found distinguishing features of the nonlinear ballistic electron transport in suspended structures. Particularly critical dc-current that suppresses commensurability oscillations of the magnetoresistance is about three times lower for suspended membranes in comparison with non-suspended structures.

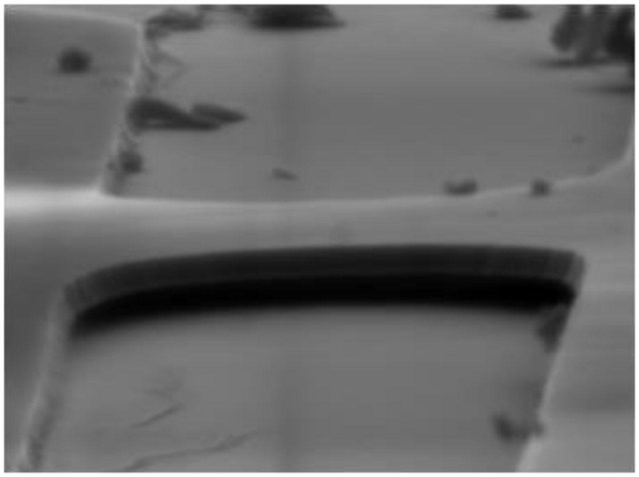

Figure 1. Membrane containing two-dimensional electron gas released from the wafer.

The work is supported by RFBR grant №13-02-01153, Program DNIT RAS project №3.2, and Presidium of RAS grant №24.19.

Wednesday, June 5

Tamm plasmon laser

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Plasmonic Tamm states are interface modes formed at the boundary between a photonic structure and a metallic layer. These modes present both the advantages of surface plasmons and of microcavities photonic modes. Tamm plasmons can be spatially confined by structuring the metallic part of the system, thus reducing the size of the mode and allowing various geometries. They are very good candidates for optimizing the emission properties of semiconductor nanostructures. We will show that lasing can be obtained for InGaAs semiconductor quantum wells embedded in a Tamm structure, constituted by a GaAs/AlAs Bragg mirror covered by silver or gold[1]. For low excitation power a strong coupling regime is observed, with formation of hybrid Tamm/plasmon exciton states. When the excitation power increases a modification of the emitting diagram appear with a strong emission at k=0 at the energy of the bare Tamm mode associated with the Tamm lasing. Moreover efficient control of the spontaneous emission of the quantum wells can be obtained if the Tamm modes are spatially confined [2] leading to a reduction of the lasing threshold.

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Nonlinear interaction of light with micro- and nanostructures in fiber waveguides

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Techniques of refractive index modification in fiber waveguides by CW ultraviolet and femtosecond infrared radiation are described. Unique photonics devices based on in-fiber micro- and nanostructures formed by these techniques are presented including fiber Bragg gratings with phase shifts, periodically poled fibers, long period gratings, diffraction interferometers. Nonlinear interaction of light with such periodic as well as random structuresis studied. As a result, new regimes of light propagation, generation and nonlinear conversionin all-fiber configurations have been obtained and explored,namelytunable single-frequency lasing,random lasing, parametricand second harmonics generation, dissipative soliton generation and its Raman conversion. Applications of the obtained results for practical purposes are also discussed.

Harnessing light with photonic wires: from needles to trumpets

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CEA/INAC, Grenoble

In the last years, photonic wire antennas have emerged as a broadband alternative to microcavities for improving the brightness of non-classical light sources based on quantum dots. I will describe recent developments leading to a trumpet-like antenna which offers in particular a Gaussian far-field emission. I will also show that photonic trumpets constitute a novel type of hybrid system, where material strain strongly couples the emission wavelength of a single quantum dot to a discrete vibration mode.

All photonic crystal laser cavities

A. Monmayrant

LAAS, Toulouse

Quantum dot mode locked lasers for coherent frequency comb generation

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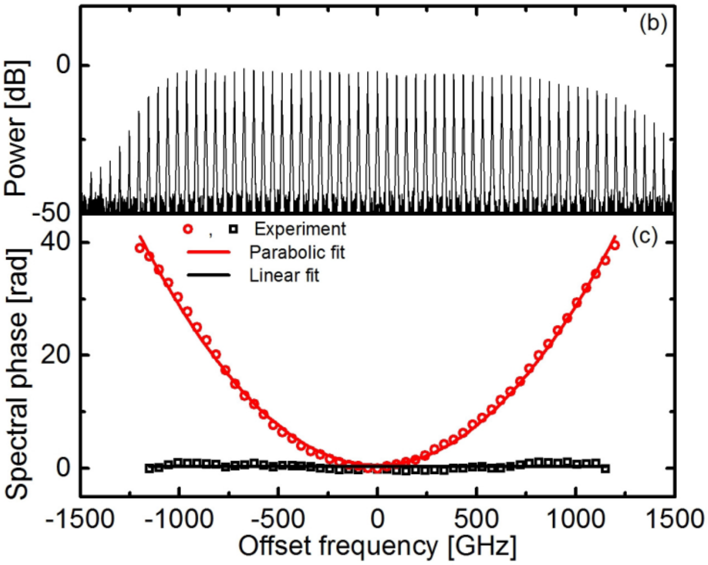
Monolithic semiconductor passively mode locked lasers (MLL) are very attractive components for many applications including high bit rate telecommunications, microwave photonics and instrumentation. The inhomogeneous gain broadening and the ultrafast absorption recovery dynamics are an asset for short pulse generation. Moreover, the weak coupling of amplified spontaneous emission with the guided modes plus low loss waveguide leads to low timing jitter. 1.55 μm InAs/InP quantum dash nanostructures, in particular, have demonstrated efficient mode locking in single section Fabry-Perot configurations. The flat optical spectrum of about 12 nm (figure), combined with the narrow RF beat note linewidth of about 10 kHz make them a promising technology for optical frequency comb generation. Coherence between spectral modes was assessed by means of spectral phase measurements. The parabolic spectral phase profile (figure) indicates that short pulses can be obtained provided the intracavity dispersion can be compensated by inserting a single mode fiber.



Surface Tamm states in two-dimensional photonic crystal made of macroporous silicon

S. Tikhodeev

PGPI RAS, Moscow

Metal-free plasmonics for infrared applications

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Surface plasmon polaritons, generated at the interface between a metal and a dielectric,present a great interest because of their potential applications in the fields of metamaterials or metasurfaces, enhanced photonic devices properties, nanophotonics integrated circuits and nano-bio-photonics. All these applications rely on the use of gold resonators. Because of the need to integrate plasmonic functionalities to semiconductor devices and to keep high field exaltation at the metal/dielectric interface for mid-IR application, it is really attractiveto use highly doped semiconductors. By changing the doping level of the semiconductor, it is possible to adjust its plasma frequency to reach the mid-IR range and tocontrol the magnitude of its permittivity for a better control of local electromagnetic field. Another advantage of using highly doped semiconductor is the fact that it is not necessary to add a layer of chromium or titanium which ensures the adhesion of the gold layer, but also introduces optical losses.

We propose an experimental study of strip arrays of doped semiconductors encapsulated in un-doped material. The samples consist of a 50 or 100 nm thick layer of lattice-matched InAsSb (Si-doped at 10^{20} cm^{-3}) grown by Molecular Beam Epitaxy (MBE) on a GaSb substrate. InAsSb arrays are realized by holography and wet or dry etching. The typical grating period is 540 nm and the width of InAsSb ribbon varies from 210 to 90 nm. The encapsulating layer of GaSb is performed by MBE on the InAsSb grating. Reflectance experiments realized by varying the angle of the incident light and its polarization allowed identifying localized surface plasmon (LSP). We will discuss the different experimental results and try to understand all the observed resonances.

Type-II interfaces of II-VI nanostructures for photovoltaics

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The motivation of this work is to take advantage, for optimizing photovoltaic conversion, of peculiarities that naturally occur at the interfaces between some semiconductors. Pairs of semiconductors are said to exhibit a so-called type-II interface, or staggered band alignment, when the maximum energy of the valence band and the minimum energy of the conduction band are located at opposite sides of the two materials interface. Excitons photo-generated in the vicinity of such an interface are then spontaneously dissociated. We will illustrated this concept with single interfaces, superlattices, and core-shell nanowires. The goal is both to go beyond the simple charge separation by a p-n junction, and to tailor the bandgap of the absorber to fit the solar spectrum (~ 1.4 eV).

Magnetic properties of metamaterials based on ferromagnetic nanocylinders

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LSPM-CNRS, UPR 3407, Université Paris 13, 99 av. J. B. Clément, 93400 Villetaneuse, France

Electrodeposited arrays of ferromagnetic nanocylinders (NCs) have been the object of intensive experimental and theoretical investigations. Such magnetic artificial materials are important class of active metamaterials needed for prospective data storage and signal processing applications.

We present static and dynamic magnetic properties of two-dimensional arrays of ferromagnetic NCs, embedded into ordered nanoporous aluminum oxide (Al_2O_3) templates investigated by means of vibrating sample magnetometry (VSM) and Brillouin light scattering (BLS) techniques, respectively. The BLS spectroscopy gives access to spin waves modes with non-zero wave vector values in the 3-300 GHz spectral frequency range. The inelastic scattering by magnetic modes allows a detailed study of the dynamics of magnetization in NCs.

The experimental results are analyzed within the frame of analytical model based on a mean-field approach including the dipolar magnetic coupling between the NCs in the array. Respective role of the direction of the applied field, of the magneto-crystalline and the shape anisotropies as well as the effect of the aspect ratio and of the packing density of the cylinders are pointed out and discussed.

Thermo/photo-switchable molecular nanomagnets based on copper-nitroxide clusters: an EPR study

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The research on molecule-based magnetism recently received significant attention due to a focus on new nanostructured materials with unusual combinations of physical properties. Electron Paramagnetic Resonance (EPR) is one of the essential tools for studying molecule-based nanomagnets, since it allows direct probing of the spin levels rather than providing thermodynamic averages as in standard magnetic measurements. In this report the applications of EPR to a new family of thermo/photo-switchable molecular nanomagnets based on copper-nitroxide clusters will be reviewed. In particular, EPR studies of these compounds allowed us to obtain values and temperature dependences of inter- and intra-cluster exchange interactions responsible for the observed magnetic anomalies. In addition, continuous wave and time-resolved EPR techniques were indispensable in the studies of photoinduced spin state switching and excited state relaxation in copper-nitroxide based molecular magnets. This work was supported by RFBR (12-03-33010, 11-03-00158) and RF President grants (MK-1662.2012.3, MK-1165.2012.3).

Magnetization reversal in self-organized epitaxial magnetic nanodots

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The understanding and control of the magnetic anisotropy and the magnetization reversal at the nanometre scale is a major challenge to tailor new magnetic recording devices. In this framework, the study of magnetic properties of self-organized systems appears to be promising as the size distribution is narrower and therefore the results obtained by averaging over a large assembly of particles are less complex to analyse [1].

In this talk, I will review our recent works on the understanding of magnetization reversal of nanometre size magnets obtained by self-organized epitaxial growth on the Au(111) surface. After an introduction to the macrospin model and its range of application [2], I will focus on the study of two model systems consisting of a 3d magnetic and a 5d non-magnetic element, namely CoAu and CoPt nanostructures. Co and Au are largely immiscible and easily realize core-shell epitaxial nanostructures. The in situ measurement of magnetic susceptibility as function of the Au capping shows that the magnetic anisotropy of the Co core is mainly due to magneto-elastic effects [3]. In contrary, Co and Pt are strongly miscible. Depending on the growth procedure, we have realized either mixed or core-shell nanoparticles. The structural parameters have been determined by Extended X-ray Absorption Fine Structure and the magnetic properties by X-ray Magnetic Circular Dichroism and Magneto-Optic Kerr Effect [4]. In this system, we have shown that hybridization effects are dominant to understand the trend in the out-of-plane magnetic anisotropy, i.e. a strong decrease in mixed particles and an increase in core-shell particles [5]. A phenomenological pair model for magnetic anisotropy is able to reproduce qualitatively these results.

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^{129}Xe NMR for porous carbon materials including Multi-wall carbon nanotubes

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Nowadays ^{129}Xe NMR of adsorbed xenon has become indispensable technique for characterization of porous materials. In this lecture we are going to discuss ^{129}Xe NMRapplicability for porous carbon materials. Due to structural disorder, distribution of the crystallite size, presence of amorphous domains, heterogeneity of surface properties, strong paramagnetic sitesthe interpretation of^{129}Xe NMR data is rather complicated for carbon materials. We have re-examined this problem for a series of microporous carbons with similar surface chemical properties and mesoporous carbons with a wide range of pore diameters and for the Multi-wall carbon nanotubes.The uses and limitations of ^{129}Xe NMR for characterisation of porouscarbon materials and carbon-based catalysts have been elucidated. Although ^{129}XeNMR exhibits definite advantages over conventional adsorption and diffraction techniques, it can hardly be referred to as an all-sufficient method. Its use as asupplementary tool, however, will be highly appreciated.

Magneto-optical properties of magnetic quantum dots and semiconductor nanowires

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The physical properties of manganese based diluted magnetic semiconductors (DMS) are dominated by large exchange interactions between localized spins and free carriers. In II-VI DMS the coupling between Mn spins and photocarriers induces a giant Zeeman effect of the excitonic lines, which can be used as an extremely sensitive probe of the Mn spin subsystem. In a first part, we will review the recent magneto-optical studies we performed on (Cd,Mn)Te magnetic quantum dots. I will discuss more specifically how single dot spectroscopy can be used to probe the local magnetization of few Mn spins [1].

In a second part, we will review the first optical studies we performed on ZnTe nanowires and on CdTe quantum dots inserted in ZnTe nanowires. Such nanowires are particularly promising for future studies in order to explore the spin properties of 0D or 1D confined carriers coupled to magnetic atoms [2]. Nanowires with typical diameters of 40 nm and typical lengths of 1 micrometer have been grown by molecular beam epitaxy using gold as a catalyst [3]. Micro-photoluminescence and cathodo-luminescence studies have been performed on isolated nanowires deposited on patterned Si substrates. Single ZnTe nanowires show sharp and linearly polarized emission lines close to the ZnTe excitonic band edge. The ensemble of CdTe/ZnTe nanowires presents sharp emission lines distributed between 1.8 to 2.1 eV at 5K. Multi-excitonic lines can be observed with single nanowire. Exciton and biexciton have been identified by analyzing the variation of the PL-intensities with the laser power and by auto and cross-correlation measurements. For the excitonic line, an anti-bunching at zero delay is observed from 5K to 100K [3].

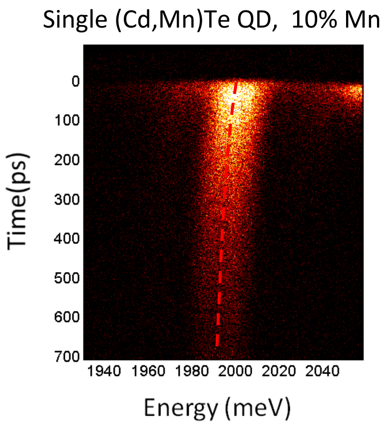

Figure 1: Time resolved .spectroscopy of a single (Cd,Mn)Te quantum dot containing 10% of Mn spins showing the formation of a 0D magnetic polaron [1]

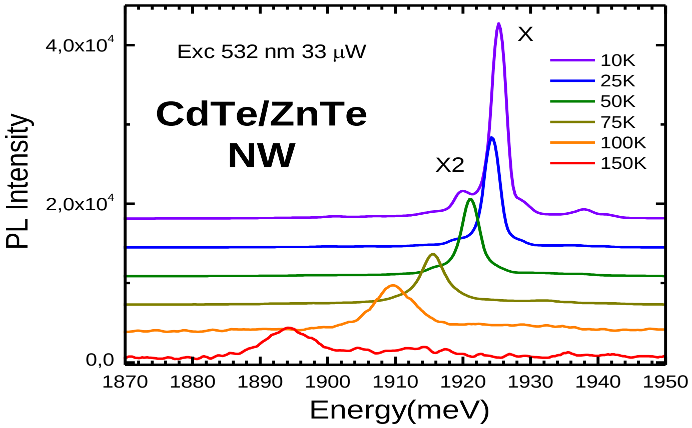

Figure 2: Exciton and biexciton lines of a single CdTe quantum dot inserted in a ZnTe nanowires. The μPL spectra have been recorded from 10K to 150K using a 532 nm laser excitation of 33 μW.

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Magnetism of nanoparticles of cobalt, iron, nickel and their alloys synthesized by pyrolysis of various precursors

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Magnetic properties of (Fe, Co, Ni) -filled multiwalled carbon nanotubes grown by chemical vapor deposition on glass substrates with a metallocene as precursor are discussed in the first part of report. The both disordered ensembles and the aligned perpendicularly to the substrate plane (Fe, Co, Ni) -filled nanotubes are investigated. Carbon nanotube is the most inert capsule for nanoparticles of Fe, Co, and Ni, as well as for their alloys. This is best solution of problem concerned with oxide shell formation that deteriorates important applied magnetic properties. The new features in the field and temperature dependences of the magnetization in (Fe, Co, Ni) -filled carbon nanotubes were revealed experimentally and discuss in the report.

The high value of coercive force is reached in equiatomic CoPt nanoparticles prepared by thermal decomposition of precursor compound $[Pt(NH_3)_4][Co(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ and it is the subject of the second report part. The correlation of magnetic anisotropy energy with order parameter at various steps of order- disorder transition in CoPt nanopowders prepared by thermal decomposition and annealed at 400°C, 500°C and 600°C for different times up to 16 hours has been studied. Particle size increases during annealing as well as order parameter, which changes from 0 in as-decomposed at 400°C CoPt nanopowder to values close to 1 after 16 hours annealing at 500°C. Coercivity and remanence increases with annealing time. The highest coercivity (14.2 kOe at 5K) is achieved after annealing. Magnetic anisotropy energy was estimated using fitting of experimental magnetization curve in high fields based on appropriate approach to saturation law. The observed correlation of magnetic anisotropy energy with order parameter is discussed in the terms of ordering domain formation and growth inside nanoparticles.

Electric field control of the magnetic anisotropy in GaMnAs-based heterostructure

A. Lemaître

CNRS-LPN, Marcoussis

We demonstrate magnetic anisotropy control and magnetization rotation in a field effect device. The device relies on a 4 nm thick GaMnAs/GaMnAsP ferromagnetic bilayer. The bilayer magnetic anisotropy is controlled by the gating induced depletion which reinforces the anisotropy contribution of one layer with respect to the other. Irreversible switching or coherent magnetization rotation assisted by the electric field is demonstrated.

Detection of nuclear magnetization by Faraday rotation

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Nuclear spin dynamics in semiconductors has been studied extensively by electrical, magnetic and optical techniques such as NMR and transport measurements, luminescence depolarization in a transverse magnetic field, time resolved Faraday/Kerr rotation [1]. Out of all these methods, the optical techniques are the most sensitive. Two of the mostly used techniques to detect nuclear spin polarization are: depolarization of luminescence in a magnetic field [2] and electron spin resonance detected by time resolved Faraday rotation. The presence of spin polarized carriers in the sample is necessary in order to observe either circular polarization of luminescence or the Larmor resonance frequency shift (Overhauser shift) due to nuclear magnetization [3]. The spin polarized electrons used for the measurement, can also provide a strong feedback, which may greatly complicate and modify the behavior of nuclear spin system [1]. Direct measurement of nuclear field induced spin splitting in QDs has been achieved by high resolution photoluminescence [4]. In this case it is not necessary to have spin polarized electrons, but still there is presence of non-equilibrium carriers. As a result, existing methods of optical detection are perturbing and/or destructing nuclear spin polarization.

In this work we demonstrate *non-destructive* detection of nuclear magnetization in n-GaAs via cavity enhanced Faraday rotation of an off-resonant light beam. We use a two-step protocol, proposed by Artemova and Merkulov [5], where preparation and measurement are separated in time. During the measurement, initially prepared nuclear magnetization is in equilibrium with electron gas and is detected via small conduction levels spin splitting, and the equilibrium electron spin polarization in the hyperfine effective field.

This detection scheme is sensitive to (i) nuclear spins situated within the localization radius of donor-bound electrons and characterized by fast dynamics, as well as to (ii) all other nuclear spins in the sample characterized by much slower relaxation rate. Contributions to the Faraday rotation related to the magnetization of different nuclear species with different localizations in the sample are identified in nuclear magnetic resonance experiments. Our results provide new insight in the mechanisms of nuclear relaxation in metallic n-GaAs: diffusion limited nuclear spin relaxation dominates over Korringa mechanism.

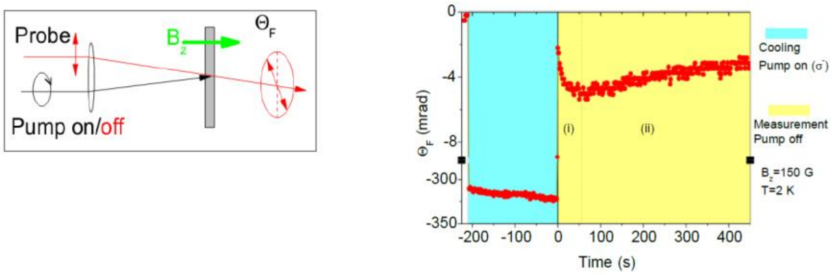

FIG. 1. (Left) Sketch of the experimental set up; (Right) Faraday rotation under optical pumping ($t<0$, σ^- polarized light, $B_Z=150$ G) and Faraday rotation induced by nuclei "in the dark" ($t>0$, $B_Z=150$ G).

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Cu_2O Nuclear Quadrupole Resonance as a stress gauge

J.-B. d'Espinose de Lacaillerie
ESPCI, Paris

Thursday, June 6

Ultimate Control of Graphene Growth

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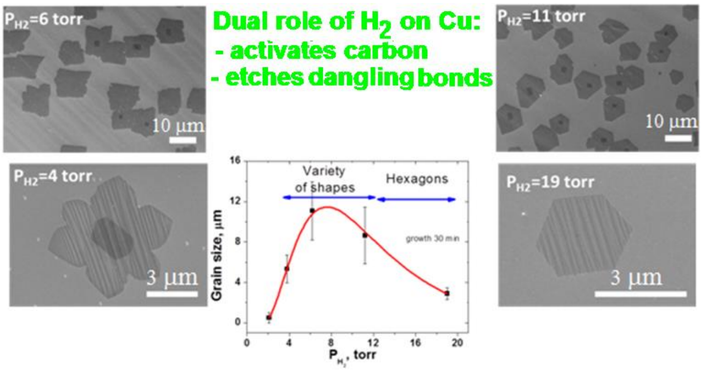
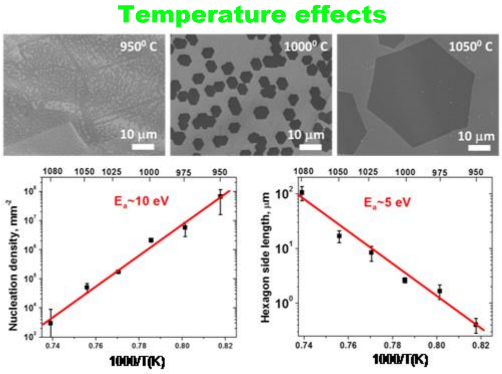
We present detailed investigation of the processes responsible for atmospheric pressure chemical vapor deposition (APCVD) of high quality graphene on metal catalysts with desired properties, e.g. single and multilayers of close to single crystal quality on large area substrates. We have demonstrated the crucial roles of temperature, metal substrate and its crystallographic orientations, co-catalyst (H_2), and the carbon source on the graphene properties. These findings should lead to design of optimized fabrication of monocrystalline graphene with different well defined number of layers that can be realized in technologically attractive roll-to-roll manufacturing.





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In-situ control of deposition process of graphene on nickel during CVD synthesis

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Chemical vapour deposition method for graphene synthesis on metal substrate is a very promising approach for fabrication of large-scale and high quality graphene film. Nevertheless the mechanism of CVD technique of graphene synthesis is still not fully understood. Thereby in this work we present the detailed investigation of CVD method of synthesis of graphene on polycrystalline nickel foils from gas mixture of methane, hydrogen and argon [1, 2, 3]. The *in-situ* measurements of resistance of nickel foil are demonstrated also in present work. These measurements allow to study and to control the process of graphene deposition on nickel substrate. Therefore it is possible to obtain the desired thickness of graphene film which can be used in variety of optical and electronic applications.

The work was supported by grants RFBR-12-02-31373 and RFBR-13-02-01354.

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Biexciton in semiconducting carbon nanotubes

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Single-walled carbon nanotubes (SWNT) are one-dimensional nanostructures where the Coulomb interactions between charge carriers are strongly enhanced compared to systems of higher dimensionality. This results in an electron-hole bound state -the so-called exciton- with a binding energy of the order of one third of the bandgap, which controls the SWNTs optical properties. As a matter of fact, the exciton-exciton interactions are particularly efficient and drive the exciton recombination and dephasing dynamics [1-3].

The investigation of excitonic complexes in semiconducting SWNTs is currently a topic of intense debate. The biexciton and the trion are expected to have a binding energy of about a hundred meVs. Whereas the trion has been recently observed, first in doped nanotubes [4] and then by means of all-optical generation [5], there has been no experimental evidence for the biexciton.

In this talk I will present our recent work reporting the observation of the biexciton in semiconducting single-wall carbon nanotubes using nonlinear optical spectroscopy [6]. Our experiments consist in a spectrally resolved pump-probe technique in SWNTs embedded in a gelatine at cryogenic temperature. Our measurements of the differential transmission spectrum reveal the universal asymmetric line shape of the Fano resonance intrinsic to the biexciton transition. For nanotubes of the (9,7) chirality, we find a biexciton binding energy of 106 meV. From the calculation of the nonlinear response, we provide a quantitative interpretation of our measurements, leading to an estimation of the characteristic Fano factor q of 7±3 . This value allows us to extract the first experimental information on the biexciton stability and we obtain a biexciton annihilation rate comparable to the exciton-exciton annihilation one.

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Ab initio study of electronic and optical properties of defective graphene

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Graphene, a two-dimensional hexagonal crystal with an atomic thickness, has attracted great interest due to its excellent mechanical, electrical, thermal and optical properties. Ideal graphene has the linear dispersion of π-bands around the K point and has the highest electron mobility of any known materials. However, it appears that graphene surface could contain structural defects which may change electronic, transport and optical properties, and this is the main concept of nanoengineering of defect structures on graphene.

Using ab initio calculations we found that band structure, DOS and dielectric function of graphene can be tuned by introduction of bending and perforation of carbon network. Another interesting case, twisted bilayer graphene, was investigated.

Transparent conductive fimls of iodinated single-wall carbon nanotubes for optoelecyronics

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K. Kaunisto[3], E.I. Kauppinen[4], H. Kataura[5], K. Suenaga[5], J.-L. Sauvajol[6]

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Many years researches are looking for materials with a high optical transparency and a low electrical resistance to create the efficient material for transparent conductive electrodes and to replace the most popular today fragile indium tin oxide (ITO). In this work we have shown that an introduction of iodine into the inner space of single-wall carbon nanotubes constituting a thin film can decrease its electrical resistance more than one order of magnitude (Fig. 1).

We have proved that the iodine species are situated inside nanotubes (Fig. 2). UV-vis-NIR optical absorption spectra have demonstrated a suppression of E_{11} band, indicating a shift of Fermi level into the valence band and metallization of all nanotubes [1]. New bands corresponding to iodide chains have observed in a low frequency part of Raman spectra. The minimal measured sheet resistance of 60 Ohm/square is comparable with that of ITO and makes the nanotubes with encapsulated iodine a prospective material for optoelectronics.

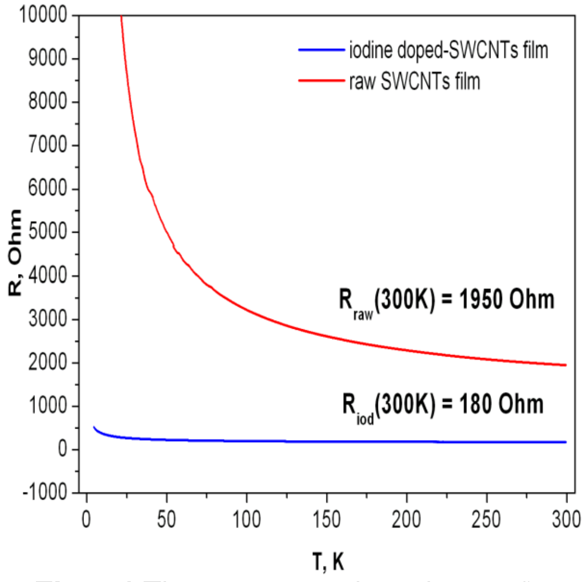

Figure 1. The temperature dependences of electrical resistance of pristine and iodine-filled single- wall carbon nanotubes.

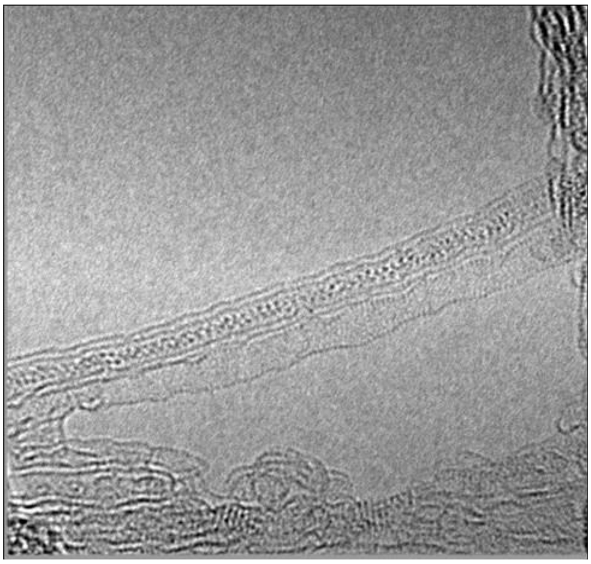

Figure 2. HRTEM image of single-wall carbon nanotubes filled with iodine.

The work was supported by RFBR 13-02-01354, MK-5618.2012.2 and IRSES 247007 projects.

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Luminescent properties of CdS quantum dots formed on carbon nanotube

A.V. Okotrub[1], L.G. Bulusheva[1], S.V. Larionov[1], A.V. Guselnikov[1], Yu.V. Fedoseeva[1], M.A. Kanygin[1], A.A. Zarubanov[2], K.S. Zhuravlev[2]

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Combination of anisotropic carbon nanotube (CNT) arrays, possessing high electrical conductivity, with semiconducting nanoparticles (NP) allows creating a new class of low-dimensional hybrid materials with unique electronic, optical and chemical properties. In this work we present synthesis semiconductor NP cadmium sulfide CdS and diamonds on CNT surface and tips. CNT arrays were grown on silicon substrates using aerosol assistant chemical vapor deposition (CVD) method. Simple and effective methods for synthesis of the hybrid material from the CdS nanoparticles NP on CNTs are proposed. The size and the shape of the CdS NP formed on CNT were found to depend on the temperature of water or other organic solutions. Electron microscopy study revealed a direct contact between CdS nanoparticles and CNT surface. X-ray photoelectron spectroscopy examination of the CdS/CNT hybrid material detected surface oxidation of the grown nanoparticles. The synthesis methods allow preserving alignment of CNTs in the array and uniform decorating the CNTs with CdS nanoparticles or deposition only on nanotubes tips. Formation of the continuous CdS/CNT interface indicates that nucleation and growth of the NP take place directly on the nanotube surface. Electroluminescent properties of synthesized materials were studied on a set-up elaborated for measurement of field electron emission characteristics. Using microwave plasma CVD reactor we growth hybrid structures diamond cristals 1 – 5 μm in size and on surface of CNT arrayes. The structure and electroluminecsent properties of new materials were investigated. The samples were examined using optical and scanning electron microscopy, Raman spectroscopy, and x-ray photoelectron spectroscopy. The field electron emission from the of new hybrid samples was compared with those from the uncovered CNT array.

Nanoporous MOFs: host-guest chemistry and material properties

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Nanoporous metal-organic coordination polymers (or MOFs) are considered to be promising for the development of the most recent problems in highly selective separation, heterogeneous catalysis, luminescent materials design and others. Herein we report the synthesis, structure and material properties of MOFs with permanent porosity, interesting guest-dependent luminescence properties and remarkable catalytic activity.

Unique example of biporous MOF with two distinct isolated 1D channels with different chemical interface is considered [1]. Co-existence of the different channels by itself broads the host-guest chemistry of such compounds so as the channels dimensions allow the size-selective guest uptake, and the distinctions between chemical behavior of the channels surfaces makes the sorption not only size-selective but governed by chemical affinity as well. Such circumstance makes biporous MOFs prominent for separation purposes.

We have reported the impregnation of the nanoporous MIL-101 structure by nonvolatile acids [2]. Such a simple approach affords solid materials with potent proton-conducting properties at moderate temperatures, which is critically important for the proper function of on-board automobile fuel cells. The proton conductivities of H2SO4@ MIL-101 and H3PO4@MIL-101 at 150 °C and low humidity outperform those of any other MOF-based materials and can be compared to those of the best proton conductors, such as Nafion.

This work was supported by the Russian Foundation for Basic Research (11-03-00112, 12-03-33033) and the State Contract (1729.2012.3).

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Author index

Научное издание

7-ОЙ РУССКО-ФРАНЦУЗСКИЙ СЕМИНАР ПО НАНОНАУКАМ И НАНОТЕХНОЛОГИЯМ

ПРОГРАММА И СБОРНИК ТЕЗИСОВ ДОКЛАДОВ

The 7th Russian-French Workshop on Nanoscience and Nanotechnologies

PROGRAM AND ABSTRACTS BOOK

Ответственный за выпуск
д.ф.-м.н. ОКОТРУБ Александр Владимирович

Техническое редактирование и верстка
Седельникова О.В., Коротеев В.О.

Подписано к печати и в свет 23.05.2013.
Формат 60×84/8.
Гарнитура «Times New Roman». Печ. л. 14. Уч.-изд. л. 13,3.
Тираж 90 экз. Заказ № 90.

Федеральное государственное бюджетное учреждение науки
Институт неорганической химии им. А.В. Николаева Сибирского отделения РАН.
Просп. Акад. Лаврентьева, 3, Новосибирск, 630090.