Book of abstracts

of the 3rd International School on Surface Science

"Technologies and Measurements on Atomic Scale"

SSS TMAS
Khosta (Sochi)
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Preface

The School's primary objective is to convey the state of the art in modern surface science and demonstrate theoretical and experimental ability to study single atoms or molecules adsorbed on solid state surfaces. First and Second Schools were successfully held in Veliky Novgorod and Khosta (Sochi) in 2011 and 2012, correspondingly. Third School will also demonstrate multiple roles of a scanning probe microscope operating at cryogenic temperatures and in ultrahigh vacuum, the main experimental tool at the atomic scale. It can be used not only as an extremely high resolution microscope but also as a multipurpose spectrometer to study the electronic, vibrational and spin states of a designated object with atomic resolution.

All School's lecturers, both Russian and International, are leading figures in their respective parts of surface science. Lecture topics center around surface magnetism, model catalysis, surface phase transitions, quantum informatics, superconductive and strongly correlated systems, and low dimensional systems including carbon nanomaterials. The School is organized as a 7-day workshop in which lectures alternate with participants' own presentations.

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Conference Program

Fluorescent metal nanodots as a special class of nanoobjects

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Fluorescent nanoclusters attract much attention as a promising tool for bioimaging and chemical sensing. Owing to their high sensitivity to environment, fluorescent nanoclusters are expected to find much applications in analytical chemistry and biology. Their high brightness and photostability also open many opportunities for various photonic applications. A large variety of strongly luminescent complexes of metal clusters with polymers, especially DNA-stabilized silver nanoclusters [1], have been reported last decade. A comparison of different approaches for the unique optical properties of polymer-stabilized metal nanoclasters will be reported. The focus will be paid to the molecular-like model in describing the absorption and emission properties of the clusters. Their electronic states may be treated as discrete energy levels leading to essentially different optical, electrical and chemical properties from nanoparticles and bulk metals. The main spectral features of the clusters such as easy tuning by the DNA base sequences, and large spectral broadening may be explained in the frame of molecular-like behavior of the emitters using the threadlike model [2].

The following points concerning chemical and physical properties of the clusters will be reported in the lecture:

1) Preparation of the clusters stabilized by polymer molecules
2) DNA-stabilized silver clusters
3) Structure and spectral properties of the clusters: experimental studies
4) Structure and spectral properties of the clusters: quantum chemical methods
5) Visualization of the clusters using confocal, STM, and tip enhanced scanning microscopy

This lecture will focus on the recent advancement of the methods available for the immobilization of the clusters on silicon, graphite, and graphene substrate using DNA by different interactions (covalent or non-covalent and insertion of DNA through graphene nanopore or nanogap), various types of assemblies, and future prospects. Furthermore, the various potential applications of the resulting new nano DNA-clusters hybrid materials are also highlighted.

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Chemistry of discharge and recharge of Li-air battery: operando XPS studies

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Highly demanded efficient energy storage is associated with lithium-air batteries. Power sources that utilize the reaction of lithium and oxygen have become a great challenge since first works in 1996 [1]. Today lithium-air batteries (LAB) attract new wave of attention due to its promise to provide more than 1 kWh/kg and skyrocketing expansion of electric vehicle market [2]. However practical use of LAB is limited by low round-trip efficiency associated with slow kinetics of oxygen reduction on discharge, oxygen evolution on charge and variety of side reactions. Further development requires understanding of the mechanisms driving the electrochemical reactions at the positive electrode. Nowadays efforts are focused on different carbon electrode materials.Recently it was demonstrated that carbon electrodes could hardly provide conditions for truly reversible reactions and efficient battery operation [3]. Rather contradictory data showing very high recharge efficiency and cycleablity of a battery with carbon electrode was also published last year [4]. In general, the lack of rechargebility is associated with Li_2CO_3 byproduct formation.It appears at the cathode due to lithium superoxide (electrochemical intermediate) or peroxide (discharge product) reactions with the carbon (electrode material). Advanced *operando* analysis of the processes at the cathode is highly useful in order to resolve such situations and facilitate the search of proper electrode materials [5]. Using operando high pressure XPS experimentswe show that superoxide radicals generated at the cathode during discharge react with carbon that contains activated double bonds or aromatics to form epoxy groups and carbonates, which limits the rechargeability of Li−O_2 cells. Carbon materials with a low amount of functional groups and defects demonstrate better stability thus keeping the carbon will-o'-the-wisp lit for lithium−air batteries.

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Spin filter effect in ferromagnetic/semiconductor structures: towards an optical spin-detection with spatial resolution

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We proposed and developed a new method of the electron spin detection by measuring the cathodoluminescence intensity from injected spin-polarized free electrons into the Pd/Fe/GaAs(001) structure with InGaAs quantum wells near the heterojunction. This method is based on the measurement on the light emitted from the recombination of the electrons transmitted through a ferromagnetic metal/semiconductor junction. The spin-filtering effect in the ferromagnetic thin layer introduce the spin selectivity so that a simple detection of the luminescence light intensity emitted from the semiconductor provides an asymmetry proportional to the incident electron beam spin-polarization. With respect to the analogue current detection technique of the spin filtering effect in metal/semiconductor junctions, optical measurement may provide significant advantages for a number of applications since it only requires to contact one of the two junction terminals, it is insensitive to the rectifying properties of the junction and it is compatible with photon counting techniques. Moreover, unlike structures where a light detector is integrated, such optical detection techniques could also allow the development of a 3D spin polarimeter for spin imaging applications. Finally, the measurement of the degree of circular polarization of the luminescence light may provide a supplementary information on the transmitted electron spin polarization. The proposed spin-detectors can be integrated in the current path registration hemispherical electrostatic analyzer with possibility of simultaneously detecting of angular and spin distribution of photoemitted electrons.

Interface architecture and electronic structure of novel graphene-based systems

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Due to unique electronic properties graphene became a perspective material for future electronics. However, low concentration of charge carriers and zero band gap of pure graphene prevent it from direct use in electronic devices. Therefore, many research efforts are focused at the elaboration of methods for inducing a band gap in graphene and manipulating charge carriers type and concentration. We have demonstrated that chemisorption of atomic hydrogen on graphene, gives rise to changes in the electronic properties and induces a gap in graphene's electronic structure [1-2]. Another promising approach for modifying the electronic properties of graphene is doping with heteroatoms. We have developed reliable procedures for graphene doping with boron or nitrogen atoms, which allows to select p- or n-type conductivity and control charge carriers concentration [3,4]. Here we discuss the dependence of the electronic doping effect on the dopant concentration and demonstrate the impact of graphene defects on the charge transfer from impurities to graphene. Also the conditions for effective inclusion of impurities into graphene and for interconversion between different bonding configurations are discussed.

The other successful method for tuning the properties of graphene and its interface with the substrate is intercalation of different atoms underneath graphene. It provides possibility for varying of the strength of graphene bonding to substrate and allows tuning of the substrate composition and properties due to controlled alloying of intercalated atoms with the substrate material [5]. We demonstrate this approach by several recent examples, including formation of graphene contacts with different metal silicides, widely used in the silicon-based electronics. These results may provide a further step towards integration of graphene devices with the existing silicon technology.

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Rashba Splitting in Monolayers of Au, Cu on a W(110) Substrate

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Recently discovered effects of induced spin-orbit splitting of states in adsorbed layers of light metals under contact with heavy metals expand the list of metals which can be used in spintronics [1-4]. However, the factors responsible for this effect and value of spin-orbit splitting were not well understood up to now. In particular, the spin- and angle-resolved photoemission experiments of Au and Ag monolayers on W(110) have been analyzed recently by density functional calculations [5]. The spin-dependent dispersions of the formed in-gap states and their spin-orbit splittings have been calculated in Ref. 5 resulting in good agreement with the experiment [1]. The authors connected the higher value of the experimentally observed spin-orbit splitting for the Ag monolayer in comparison with that for the Au monolayer on W(110) with a higher asymmetry of the wave functions formed at the surface (Ag and Au) atoms.

The present work is devoted to a theoretical and experimental investigation of influence of spin-orbit coupling on the spin structure of the hybrid states formed in two-component layered systems consisting of metals with different atomic numbers: monolayers of Au and Cu on W(110). It will be shown that contact of Au and Cu with heavy metal leads to the induced spin-orbit splitting of the formed states, but which does not correlate with the atomic number of the deposited metal and is even higher for Cu than for Au. Calculations of the electronic structure including spin-orbit interaction will be analyzed for the W(110) surface separating the contributions of the W 5*d*- and 6*p*-derived states from different W layers as well as the Au 5*d*-, 6*p*-, Cu 3*d*- and 4*p*-derived states of deposited metals. The analysis performed with density functional theory calculations will reveal that the contributions of the spin-orbit interaction from W and Au act in opposite directions that leads to a decrease of the resulting spin-orbit splitting in the Au monolayer on W(110). It will be concluded that the main factor responsible for their large spin-orbit splitting is the nuclear potential gradient of W probed by the corresponding hybrid wave function at the interface.

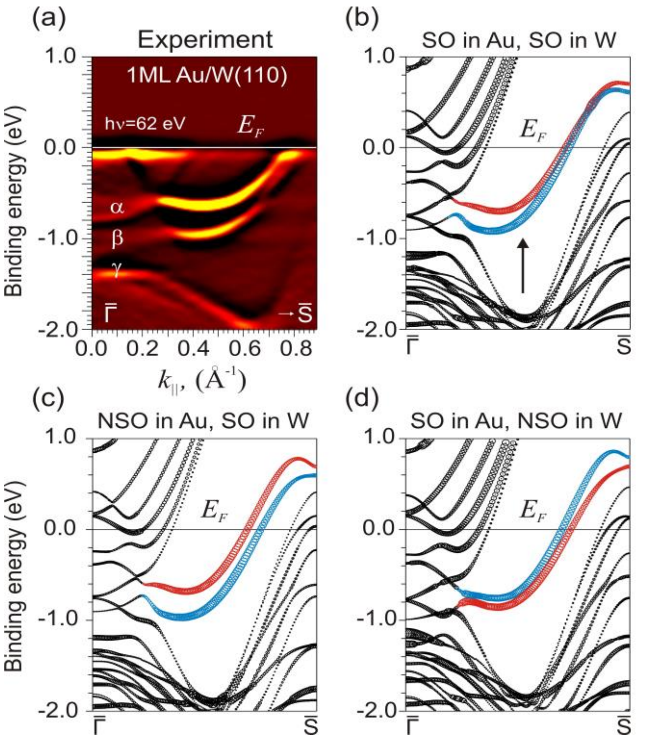

Fig. Experimental – (a) and theoretical dispersion dependences – (b) formed in monolayer of Au on W(110) which show the value and the sign of the resulting induced spin-orbit splitting of the formed hybrid states in comparison with the calculations with switching-off the spin-orbit coupling alternatively in Au – (c) and W – (d) showing the different sign of the contributions from Au and W. Blue and red colors identify the contributions of the $d_{3/2}$- and $d_{5/2}$-states, correspondingly.

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Temperature-dependence of the surface conductance of the Si(111)7×7 measured by four-point probe technique

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The temperature-dependent surface conductivity measurements of the Si(111)7×7 structure in the temperature region 35-100K were performed. The dependence of the surface conductivity follows the activation law with the activation energy 25 meV, corresponding the data obtained from STS measurements. Our results indicate the absence of any the phase transition in the temperature region from 35K to 100K.

The Si(111)7×7 is one of the most extensively studied crystal surface of semiconductors. It is known from ARPES studies [1] and theoretical band calculations [2] the surface should be metallic (the Fermi level is located inside one of the surface bands). On other hand, from STS study of the Si(111)7×7 surface properties the dielectric energy gap is observed at the surface Fermi level $2\Delta = 40\pm10$meV at $T = 5$K [3]. With the increase of the temperature the energy gap smoothly blurs and vanishes at $T > 40$K, thus providing no-zero density of surface states at Fermi level, in agreement with the general results [1, 2]. Possible scenarios of energy gap opening include Mott-Hubbard mechanism assisted by electron-phonon interaction, formation of two-dimensional Wigner crystal or density waves. The analysis of STS data shows that the energy gap vanishes mostly due to a thermal fluctuation. But more detailed study of the surface transport properties in this temperature region is necessary for understanding the origin of such behavior whether it is a phase transition or not.

This information could be obtained from the surface conductivity measurements using four-point probe technique. Here we report the results of temperature dependence of conductance of the Si(111)7×7 surface in slightly doped Si crystals with $\rho = 1\Omega$cm in the range of $T = 100 - 35$K. The conductivity measurements were performed using four-point probe with the probe spacing up to 100µm. It was shown that providing measurements at the low temperatures on slightly doped Si samples vastly reduces the bulk conductance contribution and total measured conductance corresponds to the surface.

Figure 1 shows the semilog plot of the temperature-dependence of the Si(111)7×7 surface conductance. The dependence has an activation nature. The obtained activation energy from the equation $\sigma \sim \sigma_0 \exp(-\epsilon_a/k_b T)$ is $\epsilon_a \approx 25$ meV. Such nonmetallic behavior with similar activation energy was observed in [4] at higher temperatures. The obtained data reveals no any evidence of phase transition in the temperature region T = 100 – 35K. This hopping conduction through surface-states could be proposed in terms of the localized nature of adatom dangling bonds predicted by [2]. But one should notice the good agreement in energy gap value ($2\Delta \approx 40$meV) obtained by STS and activation energy ($2\epsilon_a \approx 50$ meV). This indicates that nonmetallic behavior in both cases may have the same origin with forming some kind of electron superstructure.

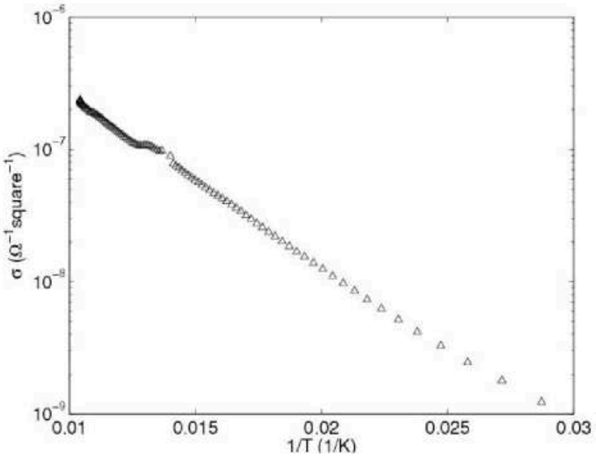

Fig. 1. Temperature-dependence of the surface conductance of the Si(111)7×7, n-type, $\rho = 1\Omega$cm.

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Photoluminescence and Raman spectroscopy of narrow graphene nanoribbons

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Narrow graphene nanoribbons (GNRs) with the width below 1.3 nm have been synthesized using confined polymerization and fusion of coronene molecules inside single-walled carbon nanotubes (SWCNTs).[1] In contrast to graphene, GNR can be a semiconductor with a large band gap. We have identified the photoluminescence response from the narrow GNRs.[2] According to our experimental results the band gap of the narrow GNRs can reach up to 2eV. The band gap of the GNR depends on its width and shape. Novel material GNR@SWCNTs has been studied by photoluminescence (PL) and Raman spectroscopies.[2, 3] GNR@SWCNTs simultaneously emit in two spectral regions. New spectral features corresponding to GNRs were detected by PL in the visible range (Figure 1). In the IR range we detect various shifts in emission and excitation of the SWCNT peak positions depending on their geometry.[3] Radial breathing modes of GNR@SWCNTs demonstrate significant shifts (up to 10 cm^{-1}) in comparison to pristine SWCNTs. Additional components within the 2D line of SWCNTs were identified after the formation of GNRs.

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

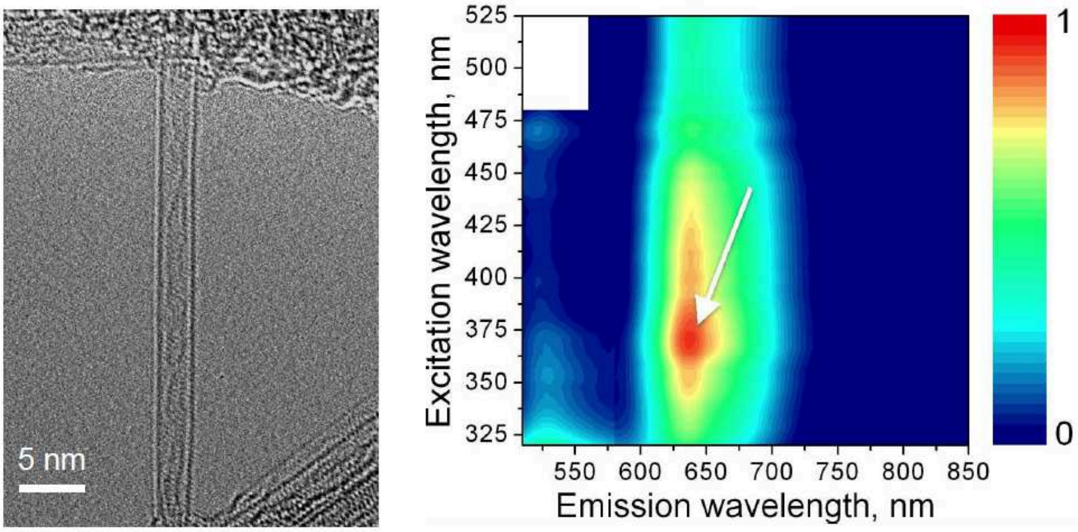

Figure 1 HRTEM image of SWCNTs with GNRs formed inside and photoluminescence contour plot in the visible range of GNRs@SWCNTs.

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Separation of Single-Wall Carbon Nanotubes by Polymer-Modified Aqueous Phases

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Single-wall carbon nanotubes (SWNTs) are one of the most exciting materials today. They appeared to be extremely useable in various fields of applications. One of the most attractive applications is utilizing nanotubes as a material for future nanoelectronics and optoelectronics. The ultimate mechanical, chemical and physical properties of SWNTs, basically, their stability upon various stress and a specific quasi-one-dimensional electronic structure and a tunability of their properties, make them perfect candidates for such high tech application areas. A high homogeneity of electronic and optical properties appears to be one of the main requirements for SWNTs. If one would like to apply nanotubes in nanoelectronics or optoelectronics a cheap and robust method of producing SWNTs with a high purity and a high homogeneity should be developed.

A SWNT separation by polymer-modified aqueous phases is a novel method of easy and cheap high quantity nanotubes separation [1]. By means of this method, one can reach a high purity SWCNT separation by a simple mixing of two polymers (PEG and Dextran) and an aqueous suspension of nanotubes with a proper amount of surfactants (SDS and SC). These polymers tend to form two aqueous phases spontaneously (concentrations of PEG and Dextran are about 8w/w % each). SWNTs are involved in the process of polymer phase formation and tend to gather in the first or second polymer according to their hydrophobic properties.

In this work we tried to separate HiPCO SWNTs into metallic and semiconducting fractions. To carry out such separation one needs to determine and mix the compounds in exact proportions. Interestingly, by adding a considerably small amount of SC, it is possible to shift equilibrium in the way that nanotubes move from the top phase to the bottom phase. The process of polymer phase formation should be carried out at about 9^0 C and it takes only 10 minutes. After the accomplishment of phase formation, the tube looks colored if SWNTs are separated (Fig. 1). According to the absorption spectra (Fig. 2) even after the first circle of separation the purity of m-SWNT is very high (over 80%) and the purity of s-SWNT is extremely high (over 99%). It is very easy to improve further the purity by a simple introduction of the separated fraction into the beginning of the new separation circle.

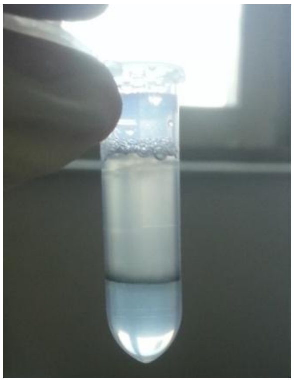

Fig.1. A plastic tube with separated SWNTs: metallic – on the bottom, semiconducting - on the top.

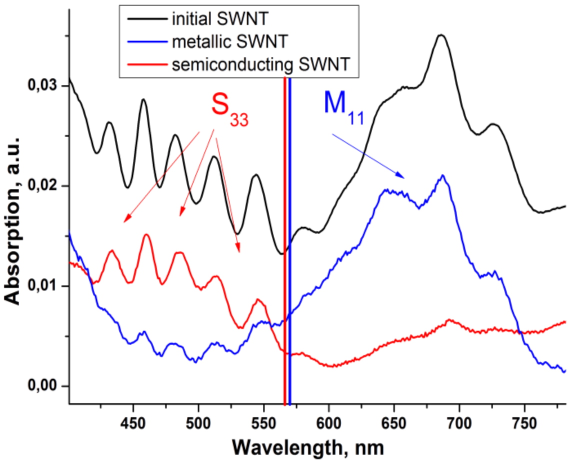

Fig.2. Absorption spectra of separated SWNT: metallic (blue), semiconducting (red) and initial fraction (black).

The work was supported by RFBR-13-02-01354 and RFBR-13-02-12181.

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DIMENSIONAL AND THERMO-INDUCED EFFECTS IN RAMAN SPECTRA OF MULTI-WALL CARBON NANOTUBES

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For the study of many nanoscale structures the method of Raman spectroscopy has been successfully used. This method is very efficient for diagnostics of various forms of carbon nanomaterials, such as single- and double-wall nanotubes, graphene, ultrafine nanodiamonds, etc. This paper presents the results of research possibilities of Raman spectroscopy for the study of multi-wall carbon nanotubes. The investigation of size and thermo-induced effects (effect of heating on the structure and process of carbonization) in the Raman spectra of multi-wall carbon nanotubes has been analyzed.

The Raman spectra were registered using “Jobin-Yvon S-3000” micro-spectrometer. Spectra were excited with the laser line with a wavelength of $\lambda = 514{,}5$ nm at low laser power to avoid heating. In the Raman spectra we have revealed the changes corresponding to the structure and characteristic modifications of materials. The basic attention has been paid to D (disorder-induced), G (graphite) and 2D (two-phonon scattering)-bands in the Raman spectra.

This research was partially supported by the RAS research programs and RFBR 13-02-90715 mol_rf_nr.

Synthesis and electronic structure of graphene heavily doped with boron

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Graphene is currently considered as a perspective material for future electronics. However, its zero band gap and low charge carrier concentration prevent it from wide implementation in electronic devices. That is why the doping of graphene to manage its polarity of conductivity and carrier concentration is necessary. Doping of graphene with boron atoms may open a band gap and make it a p-type semiconductor instead of a semi-metal. Unlike other works devoted to graphene doping [1-2] we present a different way for synthesis of graphene sheet with boron impurities.

In present work we report on the synthesis of boron-doped graphene layers on Ni(111) in a chemical vapor deposition process from carborane and propylene. In order to achieve information about the possible surface structure we prepared boron-doped graphene layers with different dopant concentrations up to 18 at.%. The chemical environment of boron was determined by X-ray photoelectron spectroscopy and X-ray absorption spectroscopy. To analyze the impact of boron doping on band structure we used the angle-resolved photoelectron spectroscopy. Boron doping leads to a shift of graphene bands to lower binding energies. This shift depends on boron doping concentration and reaches value of 0.5 eV in case of 18 at.% of boron, which may indicate notable charge transfer. Using X-ray absorption spectroscopy we have found that boron impurities are located in graphene plane. Electron diffraction together with photoemission shows that boron atoms randomly substitute carbon atoms in the graphene lattice.

This work was supported by the President's grant MK-3303.2012.2, RFBR grant 11-03-00752 and SPbSU grant 11.37.634.2013. Part of the research was carried out in resource center of SPbSU "Physical Methods of Surface Investigation".

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Atomic structure of gold intercalated graphene on Ni(111): STM study

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This work was aimed at the atomic-scale investigation of the of gold intercalated graphene on Ni(111). Graphene monolayer was grown on Ni(111) by decomposition of propene gas ($p=2\times10^{-5}$Torr) at sample temperature of 600 °C. As a result, most area of the Ni(111) surface becomes covered of the epitaxial graphene monolayer, as follows from our LEED,STM measurements and characteristic Auger spectra. The major part of the surface area is covered by (1×1) graphene, however in some areas moire-like superstructures were detected which correspond to graphene sheets rotated with respect to the Ni(111) surface.

Evaporation of 0.5 monolayer of gold onto Gr/Ni(111) surface was performed at room temperature. STM images reveal appearance of the islands(diameter 50-100 Å, height 20-50Å) associated by us with gold. The intercalation was done by annealing this system at the temperatures up to 350-550°C during several hours.

STM images of intercalated graphene shows flat islands with a triangular superstructure (characteristic for the Au/Ni(111) reconstruction) and the atomic structure corresponding to the lattice of graphene. Moreover, the graphene lattice on the intercalated islands appears to be rotated with respect to the Ni(111) lattice by the angle of 15-20 degrees. It is worth noting, that surface areas covered with (1×1) graphene remain intact even after long annealing.

Thus, we have found out that at low gold coverage (0.5 ML) the intercalation process takes place only on rotated graphene sheets. Further investigations are required to clarify the mechanism of the intercalation at higher gold coverages.

Modification of spin structure of π - states of graphene under contact with heavy metals (Bi, Au, Pt) and their joint intercalation

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Exploration of spin and electronic structure of various nanostructured systems have attracted increasing interest in recent years due to wide application in Spintronics. Typically, the valence band states of graphene are characterized by the negligible value of the spin splitting [1]. However, the results of our investigations show that the intercalation of heavy metals (Au) underneath a graphene monolayer leads to the anomalously large effects of induced spin-orbit splitting of the π-states of graphene [2-6]. Recently we have shown that synthesis of graphene on Pt(111) is also followed by enhanced spin orbit splitting of the graphene π-states. In both these cases an electronic structure is formed characteristic for free-standing graphene with linearity of π-states of graphene in the region of the K-point of the Brillouin zone. It is assumed that the effect of the induced spin-orbit splitting is developed due to hybridization of the π-states of graphene with d-states of Au and Pt and the formation of the hybridized (π-d)-states [2-6], and is related to influence of a high intra-potential gradient characteristic for atoms of Au and Pt, as heavy metals. As a result, in the region of the linearity of the dispersion dependences of π-states of graphene near the K point the Brillouin zone the induced spin splitting of π-state of graphene under contact with Au and Pt can reach the value of about 100 and 60 meV, respectively [3,5].

Thereat, if to intercalate Bi atoms underneath a graphene, any visible splitting cannot be resolved in the experiment. Bi and Au have essentially different structure of the valence band. Bi is characterized by the sp-valence band structure, i.e. the lack of valence d-electrons, which should condition for the high value of the spin-orbit splitting.

In addition to comparative study of influence of contacts graphene with different heavy metals (Bi,Au,Pt) the presented investigation is devoted to study modification of the induced spin-orbit splitting of the π-states under joint intercalation of Au and Bi underneath a graphene [6].

The modification of spin electronic structure under contact with (Bi,Au,Pt) and joint intercalation of Bi and Au has been studied by spin- and angle-resolved photoemission of the valence band electron structure (ARPES and SARPES) and core level photoemission spectra. The main factors responsible for the induced spin-orbit splitting modification under contact of graphene with heavy metals (Bi,Au,Pt) and their joint intercalation will be discussed and analyzed.

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Electronic and spin structure of topological and trivial surface states of thermoeffective topological insulator $Bi_2Te_{2.4}Se_{0.6}$

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Topological insulators are the best candidates to be key materials in future development of spintronics devices. Three-dimensional topological insulators are characterized by unique spin electronic structure with the bulk insulating energy gap and topologically-protected metallic surface states with Dirac-cone structure crossing the Fermi level. For these Dirac-like surface states the spin of the electron is locked perpendicular to its momentum in a chiral spin structure where electrons with opposite momenta have opposite spins. This peculiar SS of TIs provides a platform for fascinating quantum phenomena such as the robustness against nonmagnetic impurities and dissipation-less electronic transport [1,2]. At present, a wide class of 3D TIs has been experimentally characterized. It includes binary compounds such as Bi_2Se_3 and Bi_2Te_3, the Bi-Sb alloy, and the ternary compounds such as $TlBiSe_2$, Bi_2Se_2Te and Bi_2SeTe_2 [3,4]. In contrast to the binary compounds, Bi_2Se_2Te is characterized by a much more insulating gap resistivity. In such compounds the central layers Te(Se) in Bi_2Te_3 (Bi_2Se_3) are substituted on the layers of the second (opposite) element Se(Te).

Main aim of our work is to study electronic and spin structure of $Bi_2Te_{2.4}Se_{0.6}$ which is characterized by enhanced thermoelectric properties. In these compounds the substitution of atoms of Te on atoms of Se takes place only partially. System was investigated by angle- and spin- resolved photoelectron spectroscopy (ARPES and SARPES) with the application of synchrotron radiation and low energy electron diffraction. We have shown that this compounds belongs also to the class of TIs with the Dirac-cone surface states arranged in the region of the Fermi level and can be consider even more ideal TI that others due to an absence of significant band bending leading to pinning of the Fermi level in the region of the bulk insulating gap.

Detailed analysis of valence band and topological surface states was carried out at room and cryogenic temperatures taking into account the enhanced thermoelectric properties of $Bi_2Te_{2.4}Se_{0.6}$ [5]. It was shown that the electronic structure of this compound in also characterized by spin-polarized 2D Rashba surface states, which are localized in the local valence band gap. Spin texture of TSS and Rashba states was measured by spin- and angle-resolved valence band photoemission (SARPES) in compare with magneto-circular dichroism data measured using the right- and left- circular polarized synchrotron radiation. The results of measurements of spin electronic structure are compared with the theoretical calculations for this system. Peculiar properties of the topological compound $Bi_2Te_{2.4}Se_{0.6}$ allowed us to consider it as a perspective material in spintronics application. Possible idea for the spintronics device will be presented and discussed.

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Edge superconductivity in Nb thin film microbridges

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It is well known that so-called surface or bound states can be generated by the presence of boundaries in a material. For example, the formation of surface states for a single electron wave function in a semi-infinite crystalline lattice due to the modification of the boundary conditions was described by Tamm and by Shockley. Other examples of bound states are surface plasmons and surface acoustic waves. The formation of surface bound states for the superconducting order-parameter wave function was considered by Saint-James and de Gennes [1]. They demonstrated that superconductivity in a semi–infinite sample with an ideal flat surface in the presence of an external magnetic field H parallel to its surface can survive in a thin surface layer, even above the upper critical field H_{c2}, when bulk superconductivity is completely suppressed. Based on the phenomenological Ginzburg–Landau theory, the critical field H_{c3} for surface superconductivity, localized near superconductor/vacuum or superconductor/insulator interfaces, can be calculated as

$$1.695H_{c2}\simeq H_{c3}=H_{c3}(0)(1-T/T_{c0})$$

where $H_{c3}(0)$ is the upper critical field for surface superconductivity at temperature T=0, and T_{c0} is the superconducting critical temperature for H=0.

In our report based on ref. [2] we investigate transitions between normal state, edge and bulk superconductivity of a thin film Niobium microbridge in a perpendicular magnetic field. We use both electric transport measurements and low-temperature scanning laser microscopy (LTSLM). In particular, in the LTSLM method the bridge is placed in a magnetic field H and biased at a constant current I. Then the laser focus beam locally increases the sample temperature, probably destroys superconductivity and thus induces voltage signal. The LTSLM voltage signal as a function of the beam coordinates can be interpreted as follows: if the irradiated part of the sample was in the normal state, the laser beam induces a negligible voltage signal. However if the irradiated part of the bridge transfers a substantial part of the superconducting currents, the beam-induced suppression of superconductivity switches the whole sample from a low-resistive state to a high-resistive state.

We observe that at $H\leq H_{c2}$ the LTSLM signal at the edges of the bridge is enhanced in comparison with a signal from the inner part. It can be attributed to the depletion of bulk superconductivity with increasing H below H_{c2}. The pronounced edge signal can be explained by the suppression of the edge barrier for vortex entry/exit by the laser spot. For fields $H>H_{c2}$, the beam-induced voltage in the center of the bridge drops almost to zero while large peaks are still observed at the edges of the bridge. This apparently reflects that the bulk is no longer superconducting while the edges still contribute to a strong signal.

To explain our results and describe the resistive state of a mesoscopic superconducting thin film sample in a perpendicular magnetic field we use a simple time–dependent Ginzburg–Landau model and corresponding boundary conditions. Our numerical simulations yield the spatial distribution of the order parameter and current density for different I and H values. We model the effect of the laser beam focused on the certain position on the dc sample's resistance, assuming a Gaussian-like shape of the laser-beam-induced increase in a local temperature. These simulations are consistent with experimental results and they confirm our interpretation of LTSLM signal.

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A van der Waals corrected DFT study of the chlorine adsorption on Au(111) and Ag(111)

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Chlorine is an important element in promoting oxidation on noble metal surfaces. According to our STM measurements, chlorine forms chain-like structures on Au(111) and Ag(111) at submonolayer coverages ($\theta<0.1$ ML). In the contrast to the case of the $(\sqrt{3}\times\sqrt{3})$R30°structure (0.33 ML) characterized by the Cl-Cl distance of 5.0 Å, we detected abnormally short distances of 3.8 Å on Au(111) and 4.5 Å on Ag(111) within the chains at low coverages.

Van der Waals (vdW) interactions can influence on formation of such chain structures. In this work we present a density functional theory (DFT) study of the Cl adsorption on Au(111) and Ag(111) using semi-empirical vdW correction of Grimme (DFT-D2) [1].

As a result in case of Cl adsorption on Au(111), the vdW corrected DFT calculations have shown stabilization of single Cl adsorption at the bridge site with respect to the hcp site and also of pair Cl adsorption at the short distance (fcc-bridge with respect to fcc-fcc). Increase of attractive interaction energy at the short distance was detected. Also the formation of the chains has been tested. We calculated tree structures of four Cl atoms (fig. 1).

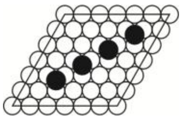
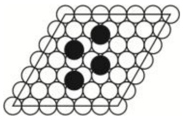
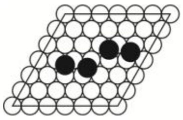
		Eads, eV/atom	
	Cl structure	PBE	PBE-D2
(a)		-0.911	-1.052
(b)		-0.909	-1.058
(c)		-0.913	-1.071

Fig.1 Adsorption energies of different Cl structures on Au(111).

The vdW corrected DFT calculations have shown stabilization of Cl chains with the short distances (fig. 1c) in good agreement with the experimental data.

In case of Cl adsorption on Au(111), the vdW corrected DFT calculations have shown stabilization of single Cl adsorption at the fcc site with respect to the hcp site. Also increase of attractive interaction energy at the short distance was detected.

Thereby, vdW corrected DFT calculations have shown significant influence of vdW interaction on Cl chain formation on Au(111) and Ag(111). Obtained results are in good agreement with the experimental data.

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Dissociative adsorption and thermal desorption of chlorine on Cu(111) surface

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In the present moment the main mechanisms of gas adsorption and desorption on solid surface are well known, but the dynamic of the reactions on atomic scale is remain insufficiently studied. In particular, the features in the thermal desorption spectra are usually explained by different adsorption positions of atoms and/or molecules, but the relation between them is not clarified enough. Reaction of Cu(111) surface chlorination is good for investigation of this problem because the atomic structures are known [1] and preliminary results of thermal desorption experiments are obtained [2]. Therefore the theoretical study of Cu(111) surface chlorination is the subject of the present work.

All calculations were carried out on the base of the density functional theory (DFT) using the Vienna ab-initio simulation package (VASP) [3]. The following stages of the reaction of Cu(111) surface chlorination were modeled: Cl_2 dissociation, chlorine adsorption, then diffusion, and finally thermal desorption of reaction products. Studied range of adsorbate coverage is from one Cl atom on clean Cu(111) surface to saturated chlorine monolayer. Energy barriers for adsorption and desorption processes are evaluated using nudged elastic band (NEB) method [4]. It was found that there is no activation barrier in the process of dissociative adsorption of Cl_2 on the Cu(111) surface, i.e. the dissociative adsorption of Cl_2 on Cu(111) proceeds spontaneously.

For all suggested models of chlorine and its' products desorption we have calculated the desorption energies and obtained desorption temperatures with a help of the Redhead formula [5]. A correlation between the obtained desorption temperatures with experimental one (peak occurs at 700K – 900K, maximum at 800 K) [2] gives an insight into interrelation of atomic structures of Cl/Cu(111) system with it's thermal desorption spectra.

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