EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

LETTER OF INTENT to the ISOLDE and Neutron Time-of-Flight Committee

Radioactive Local Probing and Doping on Graphene

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Abstract

We propose to apply radioactive ion techniques to graphene and graphene-derivated structures. Perturbed Angular Correlations will be used, to locally investigate properties associated with electron density and interactions, and using a selection of pure isotopes, dopant elements and adatoms at the graphene surface. With specific trial experiments we aim to organize and optimize procedures, to commission further equipment and strenghten the collaboration.

Requested shifts: 6 shifts, (split into 4 runs over 2 years)

1 Introduction and Motivation

Graphene presents unique physical and structural properties, and has captured the attention of a large number of researchers, as a strong candidate for a variety of electronic and energy-related devices and structures. Among the properties of graphene outstands the tunable electronic transport properties, with exceptional quantum characteristics associated to the massless Dirac fermions characteristics [1-4]. Its stiffness, stretchability and impermeability, as well as optical absorption features are also distinctive. From a technological point of view, devices like ultrahigh frequency transistors, ultrafast photodetectors, and transparent flexible

electrodes for optoelectronics were demonstrated and are being developed. The growth of graphene (single or multiple) layers on metallic and semiconducting surfaces which can then be transferred, has been achieved by several laboratories, going already beyond wafer dimensions (several cm^2) [5,6]. Moreover, the low electronic noise in graphene makes its properties very sensitive to the presence of adatoms or molecules (e.g. for sensors) and the manipulation of its properties by chemical functionalization is focus of strong attention [7-9].
In the context of condensed-matter physics, radioactive ion beams and associated nuclear techniques available at ISOLDE-CERN have been applied to modify (dope) and probe materials with the exceptional possibility to "see and feel" at the nanoscale, to determine the positions and function of all the features (atoms, electrons, electric and magnetic fields), combined with element/isotope specificity and extreme sensitivity (doses of ppm or less). It is very timely to apply these techniques to the graphene and graphene-derivated structures to locally investigate properties associated with electron density and interactions using a selection of pure isotopes, dopant elements and adatoms at the graphene surface, complementing studies that are being undertaken with other techniques and possibly reaching still unexplored features of graphene.

2 Proposed Studies

The opportunities for the application of radioactive ions in the study of graphene are numerous. With this Letter of intent we propose to start (or test the feasibility of) studies addressing on the following topics:

i) Fundamental:

a) How are the hyperfine interactions in a charged probe atom affected by the presence of a sea of 2D Dirac electrons, with a linear dispersion? Does the hybridization of a charged impurity with a completely different electronic background lead to new features? [10-12]. This is a problem related to the quantum relativistic atomic collapse in a strong Coulomb field and instability supercritical heavy nuclei atoms ($Z>170$). In graphene, the renormalization leads to a cross-over already at charges $Z\sim1$-2 predicted to produce resonances and charge screening, affecting the conductivity [13]

Perturbed Angular Correlations (PAC) is proposed to study the interaction of the probe ion nucleus and the surrounding electrons, by assessing the Electric Field Gradient and the Hyperfine Magnetic Field. Use of different valence probes is envisaged. Spin coherence relaxation mechanisms with nuclei are relevant for spintronics and quantum information processing applications [12]

b) How is the electronic structure of an impurity adatom at graphene affected and what is its influence on macroscopic properties? What controls its tunability by external control and the emergence of extended screening effects? The electronic structure of (e.g. Co) adatoms deposited on back-gated devices, could be tuned by application of voltage and screening clouds around a single atom as large as 10 nm observed [14].

Traditional techniques as electrical properties (and other available at partners) can inform on gate-controlled ionization and screening of adatoms on a graphene surface. PAC can probe local environments in the presence of additional impurities (isotopically pure) and under different electronic conditions.

ii) Applied studies:

a) Investigate possibilities of electrical/optical/magnetic/strain tuning of properties (in device structures). Perform isotopically selected studies of properties changing with radioactive isotope decay (studies along time to select a particular isotope/element half-life dependence, e.g ^{197}Hg vs ^{197}Au). Identify the origin of charge puddles with an average length scale of 20nm arising from charge-donating impurities [15] which can this way discriminated if related to a specific ion.

Radioactive transition metals would be Hg, Au, Ag, Pd, with strong spin-orbit interaction. PAC is proposed to probe the migration and localization of atoms in defects and vacancies which can be modified by strain [16, 17].

b) Locally probe with PAC the deformations of strained graphene used in flexible sensors (e.g. strain gauge, touch screens).

c) Prepare isotopically pure graphene layers or their modifications. Study of the growth on transition metal template coatings/ substrates: eg., epitaxial growth on (0001) Ru surface [18]. Graphene synthesis by ion implantation was recently demonstrated (carbon implanted at 30 keV on metal (Ni) coatings/substrates, and subsequently segregated to the surface at lower temperature) [19].

d) Graphene and graphene oxide have been investigated as new platforms for growing semiconductor nanostructures aiming diverse devices, such as quantum dots. Fundamental studies that address their nucleation are lacking. We intend to tackle this issue by monitoring the nucleation of CdS nanophases at graphene sheets. This task will involve the controlled generation of CdS seeds, in situ, using wet chemistry methods developed in our laboratories. Radioactive cadmium will be implanted in the CdS precursors and then synthetic samples will be analised for distinct reaction times to inquire the local environment of the CdS dots on the graphene surface.

Due to the exceptional characteristics of the sample, special methodologies have to be set forth to place the radioactive ions on/in the graphene sheets. At the present stage we envisage:

i) adapting the radioactive soft-landing technique used in the ASPIC facility (UHV surface purposes) after implantation of ions on metal and later evaporation onto the graphene samples surface. Also, if sufficient, perform tests using a simpler evaporator.

ii) applying the methodology of ion implantation on ice (or other frozen solvent), for later wetting of the graphene surface and ion adsorption, as used for biophysics [20]. This allows flexible means to incorporate probes, grafted (or not) to particular molecular species which attach to graphene surface allowing also functionalization studies.

iii) synthesis by ion implantation may also be an alternative to incorporate radioactive dopants and probes in the layer. The success of these procedures would determine adaptations of the future working program.

Graphene Samples

Transferable patterned graphene samples are prepared by CVD at partner laboratories [5,6]. We should anticipate the possibility of having to deal with single/double/multiple layer regions on the sample surface (at mm2 area). Growth on Cu or Ni is available.

Methodologies to be tested WITH radioactive ions incorporation:

The initial experiments will consider Perturbed Angular Correlations performed with 111mCd (T1/2 = 48m), 197mHg(T1/2 = 42m) and 111In(2.7d)/111Cd using both methods.

Methodologies to be tested with isotopicaly pure atoms:

direct implantation of ^{12}C,^{13}C,^{14}C atoms or CO_2 molecules (isotopically pure beam) on single crystals to provide source material for growth of graphene surface (technique suitable on Ru (0001) surfaces to be tested both at the off-line ISOLDE separator and on-line at ASPIC, depending on post surface treatments (sputtering) and characterization required.

In brief, we aim a LOI to start organizing the experiments, to commission the more sophisticated equipment (ASPIC) and initiate the collaboration while characterizing and optimizing initial procedures on graphene for isotopic or/and radioactive doping.

3 Summary of requested shifts:

We estimate a total of 6 shifts of beam time for this LOI in two years to allow the exploration of the largest possible of envisaged studies. In each year we ask for one to two shifts to be shared within the ^{199m}Hg and ^{111m}Cd beam times which can fit within Solid State and Biophysics collections runs, complemented possibly with parasitic collections. One will need the Biophysics collection chamber that allows implanting on ice/frozen solvent. For additional experiments with ^{111}In, we can have it from UC2 targets, during less charged periods at the end or beginning of runs.

REQUIRED ISOTOPE	ISOLDE BEAM	INTENSITY [AT/μC]	TARGET	ION SOURCE	NUMBER OF SHIFTS
^{111m}Cd	^{111m}Cd	~ 5.0E8	Molten Sn	plasma	3
^{199m}Hg	^{199m}Hg	~ 2.0E8	Molten Pb	plasma	3

Due to the nature of the sample preparation for PAC measurements, i.e., time collections of 15… 30 min per sample for ^{111m}Cd and ^{199m}Hg, each 4h, the beam time should be shared with other users.

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Appendix

Description of the proposed experiment

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the Choose an item.	Availability	Design and manufacturing
SSP-GLM chamber	☒ Existing	☒ To be used without any modification
Existing equipment on the solid state labs in building 115 - 6 detector PAC standard setups - annealing furnaces - glove boxes	☒ Existing	☒ To be used without any modification ☐ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed SSP-GLM chamber and building 115 installations.

Additional hazards:

Hazards	SSP-GLM	Building 115	[Part 3 of the experiment/equipment]
Thermodynamic and fluidic			
Pressure	[pressure][Bar], [volume][l]		
Vacuum	10-6 mbar at SSP chamber 10 during collections		
Temperature	77K due to implantations on ice.		
Heat transfer	-		
Thermal properties of materials	-		
Cryogenic fluid	Liquid nitrogen. Ice is kept at a cold finger adapted to a metallic LN2 15 litres dewar. The system is of current use since 2001, being set at the back of the SSP Chamber.	Liquid nitrogen, 1 Bar, few litres used during the PAC measurements on appropriate glass dewar.	
Electrical and electromagnetic			
Electricity	[voltage] [V], [current][A]		
Static electricity			
Magnetic field	[magnetic field] [T]		
Batteries	☐		
Capacitors	☐		
Ionizing radiation			
Target material	[material]		
Beam particle type (e, p, ions, etc)			
Beam intensity			

Beam energy			
Cooling liquids	[liquid]		
Gases	[gas]		
Calibration sources:	☐		
• Open source	☒ Produced at ISOLDE: 199mHg(42m) 111mCd (48m)		
• Sealed source	☒ [ISO standard]	22Na sources provided by RP services at CERN, used at 115	
• Isotope	199mHg(42m) 111mCd (48m)		
• Activity	199mHg < 3e7 Bq 111mCd < 3e7 Bq		
Use of activated material:	none		
• Description	☐		
• Dose rate on contact and in 10 cm distance	[dose][mSV]		
• Isotope			
• Activity			
Non-ionizing radiation			
Laser	none		
UV light	none		
Microwaves (300MHz-30 GHz)	none		
Radiofrequency (1-300MHz)	none		
Chemical			
Toxic			
Harmful		Acetone (ICSC: 0087), ethanol (ICSC: 0044) and methanol (ICSC: 0057). Less than few centilitres per chemical, used on cleaning samples on ventilated fume hood on building 115. *The respective ICSC forms have been printed and will be handled during preparation and experiments.*	
CMR (carcinogens, mutagens and substances toxic to reproduction)	[chemical agent], [quantity]		
Corrosive	[chemical agent], [quantity]		
Irritant	[chemical agent], [quantity]		
Flammable	[chemical agent], [quantity]		
Oxidizing	[chemical agent], [quantity]		
Explosiveness	[chemical agent], [quantity]		
Asphyxiant	[chemical agent], [quantity]		
Dangerous for the environment			
Mechanical			
Physical impact or mechanical energy (moving parts)	[none]		
Mechanical properties (Sharp, rough, slippery)	[none]		
Vibration	[none]		
Vehicles and Means of Transport	[none]		

Noise			
Frequency	[frequency],[Hz] Ambient noise at the ISOLDE Hall, building 170		
Intensity	Ambient noise at the ISOLDE Hall, building 170		
Physical			
Confined spaces	[none]		
High workplaces	[none]		
Access to high workplaces	[none]		
Obstructions in passageways	[none]		
Manual handling	All samples and sample holders are manually handled either by long tweezers to insert and extract the sample holder into and out of the SSP implantation chamber at GLM, or when manipulating the samples and sample holders inside glove boxes or fume houses on building 115 r-007	All samples and sample holders are manually handled either by long tweezers to insert and extract the sample holder into and out of the SSP implantation chamber at GLM, or when manipulating the samples and sample holders inside glove boxes or fume houses on building 115 r-007	
Poor ergonomics	[none]		

0.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment)*

There is no additional equipment with relevant power consumption on these small-scale experiments.