WP3 – Interfaces and nanolinks

Research strategy and methodology

WP3 occupies the intersection between the other research programmes, bridging the preparation and modification of the entry compounds (WP1 for sp^2-hybridized carbon allotropes and WP2 for sp^3-hybridized ones) and their assembly into functional, application-oriented devices. The first three activities deal with interfaces of graphene and its substrates – semiconductors, dielectric, and metal, respectively. Each of these activities focuses on a particular aspect, depending on the substrate type. A3.1 attempts to create a homogeneously flat and charged molecular interface to support graphene on a semiconductor (typically Si) or on the oxide dielectric (like SiO_2). The common foundation for the interface layers will be a molecule with a triethoxysilane covalently rooted to the substrate and a very reactive cyanate group into the space with a link of modifiable length between them (Fig. 10(i)). Depending on the purpose, a second molecule can be attached on the top: molecules with different dipoles for non-covalent support of CVD graphene or molecules with specific reactivity for particular groups decorating GO. Activity A3.2 aims at the creation and manipulation of 3D patterns in the otherwise 2D material (with or without inducing stress in it) through its mostly dielectric substrate, although similar methods will be applicable to semiconductors or metals. One route relies on prior substrate patterning to create fields of deterministically spaced and sized supporting nanostructures, typically pillars, created by E-beam lithography (Fig. 10(ii)) or grown on silicon. The test structures will be prepared using a standard E-beam lithography; however, for promising structures large-area E-beam lithography will be utilized, capable of processing 4-inch wafers or larger. The other methods combine modification of the polymer substrate before graphene transfer onto it (e.g. specific plasma treatment) and subsequent alteration with heat or laser (both for heat and photochemical reaction under the rather transparent graphene layer). Activity A3.3 tackles the generally too large contact resistivity between graphene and contacting metals by pursuing the previously suggested defect engineering of the contacted part of the graphene. The main efforts will be concentrated on the creation of linear defects, i.e. additional edges, within the graphene through various "cutting" methods (laser, ion or electron beams with or without masking). Since no method capable of fabricating atomically clean edges exists, the influence of the edge smoothness and the number of stray defects in the layer interior on the contact resistance will be investigated with respect to the used cutting method.

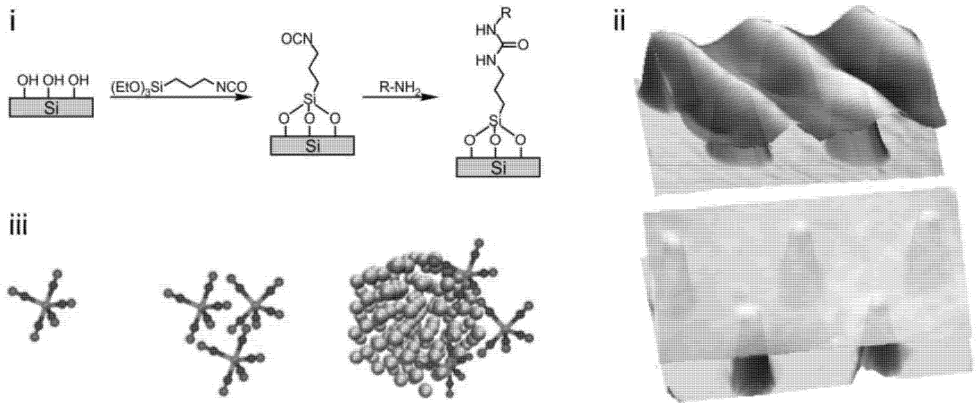

Fig. 10: i) Example of interfacial molecule for A3.1. (ii) Deformation of graphene on nanopillar array with 250 nm spacing (top) and 1000 nm spacing (bottom). (iii) Example of isolated molecule (pentacarbonyl), small cluster and small cluster on a carrier for the characterization of photochemical activity.

Activity A3.4 undertakes to covalently link the various carbon forms into a monolithic composite structure with defined porosity and composition. In general, routes for decorating the entry compounds with desired functional groups will be developed and transferred from WP1 and WP2 for graphenoids and nanodiamond, respectively. Simple linking molecules based on alkyl chains as spacers with adjustable length terminated with functional groups able to selectively couple to the functional groups on the compounds will be used according to the intended task (see the activity breakdown in the table). Also included in A3.4 – as the sole exception in the research plan strictly dividing preparation and devices - is the testing of the prepared crosslinked materials for electrochemical energy storage (supercapacitors). There are two reasons for the inclusion: (i) the energy storage application does not inherently belong to WP4 nor WP5, and (ii) it is the domain of the WP3 leading partner (UFCH). Finally, activity A3.5 will utilize the unique combination of laser and/or molecular beams accompanied by mass spectrometry to dive into the basics of the interaction between gases and model carbonaceous compounds (and their clusters, Fig. 10(iii)) to improve the selectivity of the sensors in WP4, and of the interaction between light and photoactive molecules contained in photoresists to improve the processes in optical lithography.

<table>
<tr><th>WP3:</th><th colspan="2">Interfaces and nanolinks</th></tr>
<tr><td colspan="3">Objectives</td></tr>
<tr><td colspan="3">• To increase the potential of graphene application by optimizing the graphene – substrate (semiconductor, dielectric, metal) interface.
• To synergize functional properties of nanodiamond and graphenoids in nanocomposites with covalent nanolinks.
• To realize new functional systems through combinations of carbon allotropes.
• To optimize the key involved chemical processes by using of model systems.</td></tr>
<tr><td colspan="3">Activities</td></tr>
<tr><td colspan="3">A3.1.: Molecular interface graphene – semiconductor
Duration: M1-M51</td></tr>
<tr><td>Duration</td><td>Task description</td><td>Groups involved</td></tr>
<tr><td>M1-M6</td><td>Design, formulation and synthesis of dipole molecules with the ability to be covalently linked to the Si-containing substrate.</td><td>UFCH</td></tr>
<tr><td>M3-M18</td><td>Functionalization of Si/SiO_2 substrates with dipole molecules, characterization of the functionalized substrates by surface sensitive methods (Raman spectroscopy, AFM, XPS, CPD, optical spectroscopy incl. ellipsometry, contact angle). Screening of best candidates with uniform surface coverage (both in terms of topography and dipole).</td><td>UFCH, FZU</td></tr>
<tr><td>M19-M36</td><td>Detailed characterization of graphene-covered</td><td>UFCH, FZU,</td></tr>
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	functionalized substrates (Raman spectroscopy, AFM, XPS, CPD, optical spectroscopy incl. ellipsometry, contact angle, electrochemistry incl. impedance spectroscopy, transport, impedance, and photocurrent measurement).	MFF UK, ZCU
M6-M12	Design, formulation and synthesis of molecules with the ability to be covalently linked to the Si-containing substrate as well as to functional groups in the (partially reduced) graphene oxide.	UFCH
M9-M24	Functionalization of Si/SiO_2 substrates with linker molecules, characterization of the functionalized substrates by surface sensitive methods (Raman spectroscopy, AFM, XPS, optical spectroscopy incl. ellipsometry, contact angle). Screening of best candidates with uniform surface coverage.	UFCH, FZU
M15-M32	Modification of particular types of functional groups in GO for higher selectivity of subsequent covalent linking to the substrate.	UFCH, TESLA
M25-M42	Covalent attachment of GO to the linker molecules on the Si/SiO_2 substrates and their detailed characterization (Raman spectroscopy, AFM, XPS, CPD, optical spectroscopy incl. ellipsometry, contact angle, electrochemistry incl. impedance spectroscopy, transport, impedance, and photocurrent measurement).	UFCH, FZU, MFF UK, ZCU, TESLA
M37-M51	Design and preparation of patterned functionalized (both with linker and dipole molecules) substrates using focused laser beams. Characterization of graphene-covered patterned functionalized substrates by the above mentioned methods.	UFCH, FZU, MFF UK, ZCU, TESLA
Milestone MS3.1 in M24: Uniform coverage (>95 % of area) of 1 cm^2 Si/SiO2 substrate achieved by at least for two molecules with different dipole moments.		
Milestone MS3.2 in M42: Reproducible methodology for obtaining samples of graphene and graphene oxide on organic interface-modified substrate.		
Deliverable D3.1 in M36: Summary report on the properties of graphene supported by dipole molecules covalently linked to the substrate.		
Deliverable D3.2 in M42: Summary report on the properties of graphene oxide covalently linked to the substrate.		
A3.2.: Interface graphene – dielectric with controlled deformation fields **Duration: M1 – M51**		
Duration	**Task description**	**Groups involved**
M1-M36	Design and preparation of nanopillar arrays in SiO_2 and similar substrates to induce specific orientation of deformation fields in overlying graphene. Array symmetry, pillar height, inter-pillar distance, shape and dimension of	UFCH, FZU

	the pillars' top and surface functionalization (from A3.1) will be varied.	
M3-M42	Design and growth of Si nanostructures (wires, pyramids etc.) to achieve specific deformation fields in the overlying graphene.	FZU
M19-M36	Creation of linear defects in CVD graphene before transfer by a method determined from Activity 3.3	UFCH, FZU, TESLA, MFF UK
M6-M51	Analysis of topography, strain level and orientation and charge distribution in graphene supported by the pillars or grown nanostructures (SEM, AFM, Raman spectroscopy, electrical characterization). Redesign of pillar arrays and grown nanostructures according to the obtained results.	UFCH, FZU, MFF UK, ZCU
M1-M24	Creation of deformation fields and long range topographical features in graphene by thermal processing of supporting polymers and detailed characterization (Raman spectroscopy, AFM, XPS, CPD, optical spectroscopy incl. ellipsometry, contact angle, electrochemistry incl. electrochemical impedance spectroscopy, transport measurement, impedance measurement).	UFCH, FZU, MFF UK, ZCU
M25-M51	Creation of deformation fields and long range topographical features in graphene by local laser-induced modification of supporting polymers and detailed characterization as per above.	UFCH, FZU, MFF UK, ZCU, TESLA
Milestone MS3.3 in M24: Reproducible methodology for creating 2D and 1D wrinkle patterns in polymer-supported CVD graphene.		
Milestone MS3.4 in M36: Methodology for creating 1D wrinkle patterns by artificially introduced linear defects in graphene locally supported by pillar arrays.		
Deliverable D3.3 in M24: Summary report on the properties of graphene wrinkle arrays on thermally-modified polymer substrates.		
Deliverable D3.4 in M42: Summary report on the applicability of Si grown nanostructures as support for controlled deformation of graphene		
A3.3. Interface graphene – metal with controlled defects **Duration: M1 – M51**		
Duration	**Task description**	**Groups involved**
M1-M18	Comparison of methods for graphene patterning – plasma or reactive ion etching (lithography), direct laser writing, neutron, ion, electron beams. Analysis of the defect type and their propagation from the unmasked region or focal spot, changes in the electronic structure (Raman spectroscopy, STM, AR PES).	UFCH, FZU, TESLA, ZCU, MFF UK
M19-M36	Screening of particular metal and defect combinations, measurement of the metal-graphene contact resistance	UFCH, ZCU

	(transfer length method).	
M37-M51	Optimization of the deposition and post-deposition processes (annealing) for selected metal/defect combinations. Measurement of the contact resistance, characterization of potential damage induced to graphene by the processes (Raman spectroscopy, AR PES).	UFCH, FZU, TESLA, ZCU, MFF UK
Milestone MS3.5 in M36: Selected preferred combination of defect type, patterning method and metal for further optimization of contact resistance.		
Deliverable D3.5 in M36: Summary report on the contact resistance measurement of non-optimized metal – graphene contacts.		
Deliverable D3.6 in M51: Summary report on the contact resistance measurement of optimized metal – graphene contacts.		

A3.4. Linking of graphenoids and nanodiamonds
Duration: M13 – M51

Duration	Task description	Groups involved
M13-M24	Non-selective sp^2-sp^2 linking of graphenoids (CVD graphene, GO, MWCNT) with sp^2 shell of DND, using the same functional groups on all materials. Length of the linker molecule and the utilized functional groups will be varied. Characterization of the products by Raman spectroscopy, electron microscopies, structural methods (XRD), surface area.	UFCH, TESLA, UOCHB, OZM, MFF UK, FZU
M19-M36	Selective sp^2-sp^2 linking of graphenoids (CVD graphene, graphene oxide, MWCNT) with sp^2 shell of DND, using different functional groups for each material. Creation of multicomponent mixtures with defined linking (e.g., graphene and CNT through the same functional groups, DND with different functional group). Characterization of the products by Raman spectroscopy, electron microscopies, structural methods (XRD), surface area.	UFCH, TESLA, UOCHB, OZM, MFF UK, FZU
M25-M48	Selective sp^2-sp^3 linking of graphenoids (CVD graphene, graphene oxide, MWCNT) with directly functionalized DND. Characterization of the products by Raman spectroscopy, electron microscopies, structural methods (XRD), surface area.	UFCH, TESLA, UOCHB, OZM, MFF UK, FZU
M35-M51	Formulation of composites suitable for large area deposition techniques in WP4 and their basic characterization.	UFCH, TESLA, UOCHB, OZM, MFF UK, FZU, ZCU
M37-M51	Preparation of thin film hybrid electrodes with DND covalently immobilized on CVD graphene. Characterization of the products by Raman spectroscopy, electron microscopies, AFM, structural methods (XRD), optical spectroscopy, ellipsometry, electrochemistry and	UFCH, TESLA, UOCHB, OZM, MFF UK, FZU, ZCU

	electrical characterization.	
M37 – M51	Preparation of bulk composites with high conductivity, large surface area, favourable porosity and mechanical properties for testing as supercapacitors. Material characterization with Raman spectroscopy, SEM, XRD, surface area, electrochemistry incl. impedance spectroscopy.	UFCH, TESLA, UOCHB, OZM, MFF UK, FZU, ZCU
Milestone MS3.6 in M36: Reliable methodology for the preparation of graphenoids-nanodiamond composites using sp^2-sp^2 linkers		
Deliverable D3.7 in M36: Summary report on the linking of various carbon allotropes using both selective and non-selective sp^2 links		
Deliverable D3.8 in M51: Summary report on the preparation of covalently linked sp^2-sp^3 composites and their electrochemical capacity		
A3.5. Fundamental chemical processes at interfaces **Duration: M1 – M51**		
Duration	**Task description**	**Groups involved**
M1-M12	Development of methods for the preparation of free clusters suitable as model systems for sensor interfaces (coronene, corannulene, fullerenes). Preparation of heterogeneous clusters by co-expansion as a model for carbonaceous surface and the active layer.	UFCH, TESLA, ZCU
M12-M18	Characterization of size distribution of such neutral clusters by sodium doping and soft ionization.	UFCH
M18-M36	Measurements of attachment effectivity of CH_4, CO, SO_2, NO_X on clusters. Optimization of the interface layer in order to achieve selectivity of such attachment.	UFCH
M30-M48	Application of the optimized interfaces for sensor preparation. Testing of the impedance response for different gases.	UFCH, TESLA
M24-M36	Preparation of clusters containing molecules that are photoactive in the positive photoresists (e.g., DNQ, diazonaphtoquinone and its derivatives).	UFCH
M37 – M51	Detailed study of photochemical processes in clusters at various wavelengths.	UFCH
Milestone MS3.7 in M36: Reliable experimental method for determining attachment effectivity of guest molecules on clusters, which are chemically equivalent to sensor interfaces.		
Deliverable D3.9 in M36: Summary report on measured attachment effectivity of guest molecules on clusters.		
Deliverable D3.10 in M51: Summary report on the photochemical processes in clusters containing molecules photoactive in positive photoresists.		

Milestones		
Nr.	**Month**	**Description**
MS3.1	**24**	Uniform coverage (>95 % of area) of 1 cm^2 Si/SiO_2 substrate achieved by at least for two molecules with different dipole moments.
MS3.2	**42**	Reproducible methodology for obtaining samples of graphene and graphene oxide on organic interface-modified substrate.
MS3.3	**24**	Reproducible methodology for creating 2D and 1D wrinkle patterns in polymer-supported CVD graphene.
MS3.4	**36**	Methodology for creating 1D wrinkle patterns by artificially introduced linear defects in graphene locally supported by pillar arrays.
MS3.5	**36**	Selected preferred combination of defect type, patterning method and metal for further optimization of contact resistance.
MS3.6	**36**	Reliable methodology for the preparation of graphenoids-nanodiamond composites using sp^2-sp^2 linkers
MS3.7	**36**	Reliable experimental method for determining attachment effectivity of guest molecules on clusters, which are chemically equivalent to sensor interfaces.
Deliverables		
Nr.	**Month**	**Description**
D3.1	36	Summary report on the properties of graphene supported by dipole molecules covalently linked to the substrate.
D3.2	42	Summary report on the properties of GO covalently linked to the substrate.
D3.3	24	Summary report on the properties of graphene wrinkle arrays on thermally-modified polymer substrates.
D3.4	42	Summary report on the applicability of Si grown nanostructures as support for controlled deformation of graphene.
D3.5	36	Summary report on the contact resistance measurement of non-optimized metal – graphene contacts.
D3.6	51	Summary report on the contact resistance measurement of optimized metal – graphene contacts.
D3.7	36	Summary report on the linking of various carbon allotropes using both selective and non-selective sp^2 links
D3.8	51	Summary report on the preparation of covalently linked sp^2-sp^3 composites and their electrochemical capacity
D3.9	36	Summary report on measured attachment effectivity of guest molecules on clusters.
D3.10	51	Summary report on the photochemical processes in clusters containing molecules photoactive in positive photoresists.

WP3 GANTT Chart																	
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Formulation of composites suitable for large area deposition techniques in WP4.																	

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