

Plasma Science and Technology Room: 210A - Session PS+2D-ThM

Plasma Processing for 2D Materials

Moderator: Eric Hudson, Lam Research Corporation

8:00am **PS+2D-ThM1 Low Pressure Plasma Cleaning and Doping of CVD Graphene**, *Daniil Marinov*, LPP-CNRS, Ecole Polytechnique, France, *G. Cunge*, LTM - CEA/LETI, France, *D. Ferrah*, CEA, LETI, MINATEC Campus, France, *E.V. Johnson*, LPICM-CNRS, Ecole Polytechnique, France, *J.-P. Booth*, LPP-CNRS, Ecole Polytechnique, France
INVITED

The rising importance of graphene and other 2D materials presents interesting new challenges for plasma technology. Processing of atomically thin layers requires unprecedented control of plasma parameters such as the fluxes and energy distributions of both ions and neutrals at the substrate. With sophisticated control, plasma technology can offer solutions to the major technological bottlenecks associated with graphene applications. Polymer residues (originating from the transfer of CVD graphene or from photo-resist masks) uncontrollably alter the electronic and chemical properties of graphene, a major problem for graphene integration in sophisticated devices. Removal of these surface contaminants by selective hydrogen plasma etching can perform better than classical techniques (wet chemistry with annealing) in terms of efficiency, throughput and compatibility with device fabrication processes [1]. In order to avoid plasma induced damage during graphene cleaning, the ion energy must be kept low (e.g. below 12 eV for H⁺ ions [2]). Band gap opening in graphene is another major challenge that can be tackled by plasma doping, provided that the ion energies can be controlled to favor substitutional doping rather than sputtering [3].

We are evaluating two types of plasma reactors for controllable cleaning and doping of graphene – a low density capacitive discharge excited by non-sinusoidal tailored voltage waveforms (TVW) and a high density pulse-modulated inductive plasma source. Both systems are capable of generating hydrogen plasmas with sufficiently low ion energies for low damage residue cleaning. The polymer (PMMA) etch rate obtained in the high density ICP is two orders of magnitude higher, making this system more suitable for graphene cleaning. The TVW discharge is particularly interesting for graphene doping. By changing the excitation voltage waveform in nitrogen CCP one can control the ion bombardment energy and hence the binding configuration of N dopants in single layer graphene. Using an ion bombardment energy of about 40 eV nitrogen atoms can be incorporated with a total concentration of 5 at. %, with more than half of them in graphitic sites. When the ion energy is below 20 eV only pyridinic and pyrrolic N is observed.

The role of the substrate carrying the graphene was found to be very important. In the case of hydrogen plasma treatment, ions passing through the graphene layer may participate in catalytic reactions at the substrate or lead to blister formation.

[1] Cunge *et al.* submitted to *ACS Nano*

[2] Despiau-Pujo *et al.* *J.Appl.Phys.* 2013, 113,114302

[3] Zhao *et al.* *Phys. Rev. B* 2012, 86, 165428

8:40am **PS+2D-ThM3 Sensing Cleanliness of PMMA Transferred CVD Grown Graphene**, *Christian Teichert*, *M.C. Kratzer*, Montanuniversität Leoben, Austria, *B.C. Bayer*, University of Cambridge, UK

Crystalline films of small organic semiconductors offer attractive potential for optoelectronic applications on flexible substrates. However, these applications require a transparent and flexible electrode material; and here the novel material graphene (Gr) comes into play. Since small conjugated molecules like the rod-like oligophenylene molecule para-hexaphenyl (6P) fits well to the hexagonal structure of graphene, growth of 6P on Gr can be expected in a lying configuration.

As demonstrated by in situ by low-energy electron microscopy, 6P grows at 240 K indeed in a layer-by-layer mode with lying molecular orientation on Ir(111) supported graphene [1]. Islands nucleate at Gr wrinkles [2]. At higher temperatures, needle-like 6P crystallites - also composed of lying molecules are observed [3]. Also on exfoliated, wrinkle-free graphene, such needles develop with discrete orientations defined by the Gr lattice as was detected by atomic-force microscopy (AFM) [4,5]. Needles are never observed on contaminations or on the silicon oxide substrate. There, exclusively islands composed of upright standing molecules are observed. Since these islands are easily detected by AFM, growth of 6P can be used to

sense the cleanliness of a variety of graphene substrates as we have demonstrated for PMMA transferred CVD grown graphene. On the as grown samples, PMMA remainders hinder the growth of extended needles. For increasing annealing temperature, the 6P needles grow in length because the PMMA residues decrease substantially [6].

[1] G. Hlawacek, *et al.*, *Nano Lett.* **11** (2011) 333. [2] G. Hlawacek, *et al.*, *IBM J. Res. Devel.* **55** (2011) 15. [3] F. Khokar, *et al.*, *Surf. Sci.* **606** (2012) 475. [4] M. Kratzer, *et al.*, *JVSTB* **31** (2013) 04D114. [5] M. Kratzer, *et al.*, *e-J. Surf. Sci. Nanotechn.* **12** (2014) 015303. [6] M. Kratzer, *et al.*, *Appl. Phys. Lett.* **106** (2015) 103101.

9:00am **PS+2D-ThM4 Plasma Processes of Graphene and Related 2D Materials for Energy Applications**, *L.C. Chen*, *Indrajit Shown*, National Taiwan University, Taiwan, Republic of China
INVITED

Plasma-assisted direct-growth of arrayed graphene and related hybrids will be presented. The main advantages of this type of nanostructures include high conductivity, high surface area and corrosion resistance, making them excellent candidates as electrocatalytic supports or electrodes for electrochemical (EC) energy applications, including fuel cells, supercapacitors and solar fuels. We will demonstrate the fabrication of integrated energy devices in an on-chip manner. Since the carrier transfer rate of electrode plays a crucial role in determining the energy-conversion performance, special emphases will be placed on the control of interfaces. Vertically aligned and edge-oriented graphene arrays were first synthesized by microwave plasma-enhanced chemical vapor deposition. Subsequent chemical doping can also be done in the same plasma reactor via either in-situ or ex-situ manners. Interestingly, for nitrogen doping in graphene, plasma process resulted in selective bond configuration. When applied as an EC electrode, the arrayed graphene exhibits nearly reversible redox characteristics. By varying the process parameters, samples can be produced with controllable compressive or tensile strains, which in turn show strong effects on the resultant catalytic properties.

The hierarchical graphene nanowalls can be directly grown on a variety of substrates, including Si wafers, carbon cloth as well as flexible and ultralight carbon nanofibers. The latter substrate makes such electrode an ideal portable platform having high gravimetric, areal, and volumetric electrochemical characterizations. For instance, the carbon nanofibers supported graphene-based supercapacitors exhibit excellent specific capacitance of 352.53 F/g (220.33 mF/cm²) at a specific current of 13.33 A/g, which is among the highest reported to date. Meanwhile, 99 % of Coulomb efficiency and 98 % of the initial capacitance after 10,000 charge-discharge cycles were maintained. Finally, efficient and simple routes to further attach other heterogeneous nanostructures onto graphene nanowalls have also been developed. Cyclic voltammeter studies for electro-oxidation of methanol show a high ratio of forward anodic peak current to reverse peak current, suggesting an efficient oxidation of methanol to CO₂ on the graphene-based electrode. Our approach offers a promising route toward wafer-scale fabrication of graphene not only for fundamental research but also opens up various potential applications in sensing, catalysis, as well as energy storage and production.

11:00am **PS+2D-ThM10 Engineering Chemical Functionality in Graphene**, *Sandra Hernandez*, *P.E. Sheehan*, *S. Tsoi*, *P. Dev*, *J.T. Robinson*, *C. Junkermeier*, *K.E. Whitener*, *W.K. Lee*, *T.L. Reinecke*, *S.G. Walton*, Naval Research Laboratory

Graphene has attracted enormous attention due to its unique properties. Equally important is the ability to further tailor these properties through modification of select attributes such as surface chemistry, number of layers, sheet width, and edge structures. Manipulating the surface chemistry of graphene is important since the chemical composition strongly impacts the electronic properties as well as chemical reactivity both globally and locally. Precise control of the surface chemistry of graphene can also allow for subsequent surface procedures focused on band gap engineering, device fabrication and sensor applications. Given the strong impact of adsorbates, global chemical modification provides opportunities towards greater control over the properties of graphene films. Control over the spatial distribution of these groups provides an even greater functionality in that the local graphene reactivity can be manipulated, opening up a wealth of opportunities in biosensing, plasmonics, catalysis, smart surfaces, and heterojunction devices.

Using the unique attributes of electron beam generated plasmas to manipulate the chemistry of graphene and employing patterning techniques to regulate the spatial distribution of various functional groups on the surface, we demonstrate further abilities to govern surface properties. Spatial control over structural and chemical changes is characterized through micro (m-Raman and high-resolution x-ray photoelectron

spectroscopy (XPS) mapping and electrical measurements are used to determine how local changes in chemistry influence the electronic properties. Lastly, we show that the resulting chemical moieties can be used to manipulate the local surface reactivity of graphene, enabling programmable, site-specific electrochemical deposition. These findings demonstrate the ability to tailor the locality of the surface chemistry on graphene surfaces opening up a wide range of reactivity studies and synthesis capabilities, such as programmable material deposition.

11:20am **PS+2D-ThM11 Formation of Aromatic Nitrogen Groups in Graphene Films by Post-Growth Treatment in Late-Afterglows of Nitrogen Microwave Plasmas**, *Luc Stafford*, Universite de Montreal, Canada

Graphene films were exposed to the late afterglow of a reduced-pressure N₂ plasma sustained by microwave electromagnetic fields. X-ray photoelectron spectroscopy (XPS) shows that plasma-generated N atoms are incorporated into both pyridinic and pyrrolic groups, without excessive reduction of sp² bonding. Nitrogen incorporation was found to be preceded by N adsorption, where N adatom density increased linearly with treatment time while aromatic nitrogen saturated. This finding was confirmed by Raman spectra showing a linear increase of the D:G ratio attributed to constant surface flux of plasma generated species.

Combined Density Functional Theory calculations with a Nudged Elastic Band (DFT-NEB) approach indicate that incorporation reactions taking place at point vacancies in the graphene lattice requires an activation energy in the 2-6 eV range, but the energy required for the reverse reaction exceeds 8 eV. Stable nitrogen incorporation is therefore judged to be defect-localized and dependent on the energy transfer (6 eV) provided by N₂(A)-to-N₂(X) metastable-to-ground de-excitation reactions occurring at the late-afterglow-graphene interface.

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