

Wednesday Afternoon, November 12, 2014

Plasma Science and Technology
Room: 305 - Session PS+2D-WeA

Plasma Processing for 2D Materials, Coating, and Surface Modification

Moderator: Colin Wolden, Colorado School of Mines

2:20pm **PS+2D-WeA1 Hydrogen Plasmas Processing of Graphene, Emilie Despiau-Pujo, A.O. Davydova, G. Cunge, LTM, Univ. Grenoble Alpes/CNRS/CEA-Leti Minatec, France, L. Magaud, Institut Neel, Univ. Grenoble Alpes/CNRS, France, D.B. Graves, University of California at Berkeley**

INVITED

The successful development of graphene-based technologies relies on our capability to grow and integrate this new material into sophisticated devices. Since the presence of multilayers or defects/contaminants on the graphene surface can significantly degrade its intrinsic properties, the development of new techniques to clean graphene surfaces from polymer residues, etch graphene films layer-by-layer or pattern graphene nanoribbons (GNRs) with minimal edge disorder, are major challenges. ICP H₂ plasmas seem promising to specifically treat graphene films but little is known about the fundamental mechanisms of plasma-graphene interaction. We therefore develop Molecular Dynamics (MD) simulations, coupled with experiments, to assist the development of plasma processes to clean, dope and pattern graphene layers in a controlled way. We more specifically investigate the interactions between hydrogen plasmas and various types of graphene surfaces (monolayers, multilayers, nanoribbons). Except for impacts at GNRs edges or defects location, H species are shown to experience a repulsive force which prevents any species with less than ~0.6eV to adsorb on the graphene surface. H⁺ bombardment in the [1-10] eV range does not damage the graphene basal plane while irreversible damages are expected for E_i > 12 eV (penetration of atomic H through the layers or C-C bond breaking) [1]. As a first step to model graphene cleaning, we investigate the mechanisms of CH₃ groups (a crude approximation for resist residues) removal from graphene by atomic hydrogen. Depending on the incident energy range and the surface temperature, MD shows the possibility for chemical etching of the methyl radical without damaging the graphene basal plane [2]. Recent experiments and XPS/AFM/Raman measurements confirm that H₂ plasmas are promising to clean PMMA residues from graphene with almost no damage after annealing. Simulations of GNRs trimming show that lateral etching is maximum for surface temperatures ~600 K and occurs via a specific mechanism limiting the edge roughness, as also observed experimentally. Finally, energetic H⁺ or H₂⁺ bombardment of stacked multilayer graphene (s-MLG) is investigated and the possibility to store hydrogen (trapped as H₂ molecules) between adjacent layers or etch a full single graphene sheet is discussed. [1] Despiau-Pujo, Davydova, Cunge et al, J.Appl.Phys.113, 114302 (2013) [2] Delfour, Davydova, Despiau-Pujo et al, submitted to Phys.Rev.B (2014)

3:00pm **PS+2D-WeA3 Plasma Synthesis of WS₂ Films, Rachel Morrish, C.D. Sentman, T. Haak, C.A. Wolden, Colorado School of Mines**

Two-dimensional metal dichalcogenides (WS₂, MoS₂) have attracted great interest due to their extraordinary optical properties, catalytic performance, and electronic structure. Synthesis of WS₂ has been accomplished by a variety of methods, but the high temperature (> 800 °C) and/or harsh S atmosphere required by many of these procedures precludes deposition onto conductive layers and low-temperature glass substrates needed for many applications. Previously we demonstrated the advantages of plasma processing for low temperature synthesis of a related metal dichalcogenide, pyrite (FeS₂). It was shown that stoichiometric FeS₂ films could be fabricated either by plasma-assisted sulfurization of hematite [1] or by direct deposition using pulsed plasma-enhanced chemical vapor deposition (PECVD) with mixtures of H₂S and Fe(CO)₅. [2] In this talk we describe how these two approaches may be readily extended to the synthesis of WS₂ using WO₃ and W(CO)₆, respectively.

Thin tungsten disulfide (WS₂) films were prepared on FTO coated glass substrates by H₂S plasma sulfurization of sputtered WO₃. The reactive environment provided by the plasma enabled the complete transformation of oxide films to stoichiometric WS₂ within one hour at 500 °C. An apparent activation energy of 63.6 ± 1.9 kJ/mol was calculated for the plasma conversion process, which is less than half the barrier reported for the reaction of WO₃ with H₂S. The conversion followed Deal-Grove behavior, with the growing WS₂ overlayer hindering diffusion to/from the reactive interface. Calibrated light absorption and relative intensity of the second order Raman 2LA(M) peak were identified as two additional

methods to progressively monitor the thickness of the WS₂. The semiconducting WS₂ layers exhibited *n*-type behavior with an indirect band gap at 1.4 eV and an absorption coefficient of ~5 × 10⁴ cm⁻¹. Self-limiting growth of WS₂ thin films was accomplished by pulsed PECVD with continuous delivery of tungsten hexacarbonyl diluted in a mixture of H₂S and argon. The growth rate per cycle was controlled between 0.1 – 1 Å/pulse by adjusting the precursor flowrate. It was found that the morphology and orientation of the films was a complex function of film thickness, substrate temperature, and plasma parameters. Preliminary electrochemical measurements showed that these WS₂ films reduced the overpotential required for the hydrogen evolution reaction by several hundred mV relative to FTO while displaying good stability.

[1] R. Morrish, R. Silverstein and C. A. Wolden, *JACS* **134** 17854 (2012).

[2] C. D. Sentman, M. O'Brien and C. A. Wolden, *JVSTA* **32** 021201 (2014).

3:20pm **PS+2D-WeA4 Decoration of Graphene with Gold Alloy Nanoparticles Synthesized in Solution Plasma, Maria Antoaneta Bratescu, Aichi Science and Technology Foundation, Nagoya University, Japan, T. Ueno, N. Saito, Nagoya University, Japan**

In order to be used in electronics and optics, graphene must be in contact with other materials, which can change its electrical and optical properties. The substrate, charge impurities, doping with chemical functional groups, and metal contacts can shift the position of the Fermi level of graphene. Furthermore, graphene with plasmonic nanoparticles (NPs) can offer a new perspective for light conversion systems, by optimization of visible light absorption via the SPR of the NPs, followed by electron exchange between graphene and NPs and electron transport through graphene.

In this work we present a facile, one-step, and surfactant-free method for the synthesis and loading of stable gold and gold-alloy NP on large-area graphene without NP deterioration using an electrical discharge in a liquid solution, termed solution plasma (SP). We investigated the charge transfer process between graphene and gold-alloy NPs by Raman spectroscopy and electron energy loss spectroscopy (EELS) in high resolution transmission electron microscopy (HRTEM).

The excess charge on graphene caused by transferred electrons or holes from the NPs to graphene was calculated from the change of the Fermi level relative to the initial position and the shift of the G band. In the case of graphene with gold NPs a decrease of the surface charge concentration with -3.5 × 10¹² cm⁻², and a movement of Fermi level with -0.06 eV.

In the case of the AuIn and AuGa NPs the transfer of electrons from graphene to the gold-alloy NPs produces an increase of the surface charge with 1.3 × 10¹² cm⁻² and 1.9 × 10¹² cm⁻², which correspond to a raising of Fermi level with 0.02 eV and 0.03 eV, respectively.

The EELS results were consistent with Raman spectroscopy results, i.e. the electrons and holes are transferred from the gold and gold-alloy NPs to graphene, respectively.

M.A. Bratescu, et al., *J. Phys. Chem. C* **115** (2011) 24569

S.P. Cho, et al., *Nanotechnology* **22** (2011) 455701.

M.A. Bratescu, et al., *J. Alloys and Compounds* **562** (2013) 74

M.A. Bratescu, et al., *J. Phys. Chem. C* **117** (2013) 26804

4:20pm **PS+2D-WeA7 Generation and Stabilization Mechanisms of Free Radicals in Plasma Polymers, S. Ershov, F. Khelifa, P. Dubois, Rony Snyders, University of Mons, Belgium**

Cladded aluminum alloys are widely used in many applications being protected by a conversion coating based offering some self-healing properties nowadays based on the use of toxic chromate compounds. For both environmental and work safety reasons it is necessary to identify an alternative to this chromate-based conversion coating (CBCC).

In this context, in the framework of a collaborative project, we are working on the replacement of the CBCC by a multilayer combining, among others, plasma polymer films (PPF) and conventional polymers. The key features of this multilayer is grafting of a conventional polymer on the alloy surface by using the free radicals present in the as-deposited PPF as initiating sites for a radical-based polymerization reaction. It is therefore necessary to get a complete understanding on the generation and stabilization of the PPF radicals in order to control the grafting procedure.

The aim of this work is to contribute towards the understanding of the free radicals generation mechanism in the PPF and on their stabilization by comparing the plasma polymerization of different precursors namely isopropanol, benzene and cyclohexane. *In situ* FTIR spectroscopy and a combination of XPS and chemical derivatization measurements are used to quantitatively evaluate the plasma and thin films chemistry, respectively.

Grafting experiments with 2-ethylhexyl acrylate (EHA) allows to cross-check the relevance of the XPS results.

Our results reveal that, for isopropanol PPF, the surface density of free radicals is about $\sim 1.6 \cdot 10^{14}$ spin/cm² and depends strongly on the injected power in the plasma. On the other hand, a significant effect of the presence of resonant structure in the plasma polymer on the radical stability is highlighted.

4:40pm **PS+2D-WeA8 Simulation of Direct Current Microplasma Discharge in Carbon Dioxide at High and Intermediate Pressures**, N. Hasan, P.R. Fernandez, Bakhtier Farouk, Drexel University

Direct current (DC) micro-plasma discharges in intermediate to high pressure (10–200 kPa) carbon dioxide are investigated for potential applications in carbon dioxide decomposition and thin film deposition. Numerical simulations are performed using a hybrid CFD model. The model contains detailed reaction mechanisms for the gas-phase discharge and the surface reactions to predict the species densities in the discharge and the deposition characteristics and its growth rate. Sixteen species and a seventy-six step reaction mechanism are considered for the gas-phase carbon dioxide discharge. A simplified surface chemistry consisting eleven reaction steps are considered in the model. The simulations are carried out for a DC pin-to-plate electrode configuration with an inter-electrode gap of 500 μ m. An external circuit is also considered along with the discharge model and surface reactions. Basic plasma properties such as electron and species density, electric field, electron temperature and gas temperature are studied. Special attention is devoted to study the influence of operating pressure and discharge current on the plasma characteristics and the deposition characteristics and its rate. The CO₂⁺ and O⁻ concentrations are found to be the dominant ions in the plasma. The simulations indicated significant gas heating in the entire regime of operation. Ion Joule heating was found to be dominant in the sheath whereas Franck–Condon heating and heavy particle reaction induced heating was dominant in the volume. The results presented here can be utilized for the development of computational models for plasma discharge in supercritical conditions which can be used to investigate processes such as carbon nanotube synthesis, biological reaction catalysis and carbon dioxide decomposition.

5:00pm **PS+2D-WeA9 The Impact of Ambient Gas Chemistry on Lipopolysaccharide Deactivation and Polymer Modification by Plasma-Generated Radicals at Atmospheric Pressure**, Elliot Bartis, A.J. Knoll, P. Luan, C. Hart, University of Maryland, College Park, D.B. Graves, University of California, Berkeley, I.V. Adamovich, W. Lempert, The Ohio State University, J. Seog, G.S. Oehrlein, University of Maryland, College Park

In this study, lipopolysaccharide (LPS) -coated silicon substrates were exposed to the effluent of an atmospheric pressure plasma jet (APPJ) under a controlled environment to examine the effect of plasma-generated reactive species on the surface chemistry and biological activity. The goal of the present work is to understand the role of plasma-environment interactions in biodeactivation and surface modifications by regulating both the proximity of the plasma to the environment and the environmental gas chemistry. The APPJ is mounted inside a vacuum chamber that can be evacuated and refilled with any gas chemistry. By changing the APPJ geometry, the plasma plume can be either exposed or protected from the ambient. By adding small N₂/O₂ admixtures to Ar, we find that the O₂ admixture in the APPJ is a major determining factor for both deactivation and surface modification as measured by an enzyme-linked immunosorbent assay and x-ray photoelectron spectroscopy, respectively. N₂ admixture without O₂ causes minimal deactivation, while N₂/O₂ admixtures deactivate more with increasing O₂ content. For identical O₂ feed gas flows, less deactivation occurs when N₂ is also added, which demonstrates that nitrogen-based species quench reactive oxygen species (ROS) responsible for biodeactivation. After plasma treatments, a new chemical species was detected on LPS surfaces that was stoichiometrically verified as NO₃. To determine if this species forms due to nitrogen and oxygen found naturally in LPS, we treated model polymer films of polystyrene, polypropylene, and poly(methyl methacrylate), as these materials contain solely carbon or only carbon and oxygen. We find that the formation of NO₃ is generic to all surfaces even with no N₂ in the feed gas. Thus, the reactive interaction of oxygen-based species with ambient N₂ takes place, indicating that plasma-environment interactions create this moiety and providing insight into the mechanisms by which the APPJ modifies surfaces. For polystyrene films, oxygen uptake is dramatic with O/C ratios as high as 0.47 at the near surface. The oxygen uptake results in a variety of moieties including C-O, O-C-O, C-O-NO₂, O-C=O, and O-(C=O)-O. APPJ treatments are also compared with a corona discharge to examine the role of long lived species such as ozone and NO_x. Results from gas-phase characterization will also be discussed. The authors gratefully acknowledge financial support by the US Department of Energy (DE-SC0005105 and DE-SC0001939) and National Science Foundation (PHY-1004256).

5:20pm **PS+2D-WeA10 Modification of LDPE Induced by an Ar/H₂O Plasma: Comparison between a Post-Discharge Treatment and a DBD Treatment**, Stephanie Collette, Université Libre de Bruxelles, Belgium, V. Cristaudo, Université catholique de Louvain, Belgium, T.R. Dufour, Université Libre de Bruxelles, Belgium, P. Viville, Université de Mons, Belgium, A. Delcorte, Université catholique de Louvain, Belgium, F.A.B. Reniers, Université Libre de Bruxelles, Belgium

The study of the water reactivity in plasma was achieved by injecting water vapor in the post-discharge of an RF plasma torch and in a dielectric barrier discharge (DBD), both supplied in argon as carrier gas.

The RF plasma torch operates at atmospheric pressure. Optical emission spectroscopy (OES) and mass spectrometry evidenced the production and the consumption rates of Ar, O, OH, O₂⁺ and N₂ species. These species could be quantified as a function of the water vapor flow rate, the treatment time and the gap (distance separating the post-discharge from a solid surface) to have a better understanding of the reactivity. Some chemical reactions occurring within the post-discharge could be evidenced and their importance was determined according to their kinetic constants. The reactivity of H₂O in the post-discharge was also carried out using an indirect method: the exposure of low density polyethylene (LDPE) samples to the plasma torch, in order to correlate the amount of oxygenated radicals resulting from water vapor dissociation reactions with the amount of oxygenated functions (C-O, C=O, COO) grafted on the surface. The modified LDPE surfaces were characterized by X-ray photoelectron spectroscopy (XPS), with a special emphasis on the deconvolution of the spectral envelope of the C1s peak. For longer treatment times, we showed that the decrease in the oxygen concentration observed by XPS could result from a competition between the LDPE surface etching and its functionalization. Besides, depth profiles achieved with XPS evidenced the diffusion of O in the subsurface, thus proving the efficiency of the plasma treatment. Those results were correlated with WCA measurements indicating a decrease of the angle from 100° to 35° and with AFM showing an increase of the RMS roughness value from 30 nm to 90 nm. ToF-SIMS analyzes were also achieved on LDPE surfaces. To compare the impact of the plasma treatment to the influence of water contained in the atmosphere, D₂O was injected in the plasma torch. The use of D₂O permits to selectively probe the presence of fragments from the injected water grafted on the LDPE surface.

Those results were compared to those obtained with a second plasma source, namely a DBD operating at atmospheric pressure. In this case, LDPE samples were placed directly between the two dielectric barriers. Similar species as those described in the post-discharge have been evidenced by OES and MS with however slightly different reactive mechanisms, thus explaining why the treated LDPE surfaces present a different hydrophilic state.

This work was supported by PSI-IAP 7(plasma surface interactions (Belgian Federal Government BELSPO agency)).

5:40pm **PS+2D-WeA11 Atmospheric Plasma Polymerization of Fluorinated Precursor : Comparison of Various Liquid Precursors and Plasma Types (AC and Pulsed DC)**, J. Hubert, Nicolas Vandecasteele, Université Libre de Bruxelles, Belgium, C. Poleunis, Université catholique de Louvain, Belgium, J. Mertens, Université Libre de Bruxelles, Belgium, A. Delcorte, P. Bertrand, Université catholique de Louvain, Belgium, F.A.B. Reniers, Université Libre de Bruxelles, Belgium

The deposition of PTFE like films by argon atmospheric plasma using various precursors, liquid at room temperature, is presented. Those compounds are: Perfluorohexane (C₆F₁₄), a fully saturated monomer, perfluoro(2-methylpent-2-ene) (C₆F₁₂) containing one unsaturated bond and Perfluorotributylamine (C₁₂F₂₇N), containing a central nitrogen atom to which 3 fully saturated perfluorobutyl chains are attached. The influence of the monomer structure as well as the electrical parameter of the plasma (AC or pulsed DC) on the films chemistry and deposition rate is studied.

PTFE like films are of interest because of their low surface energy which gives them interesting properties such as easiness of cleaning etc.

The surface composition of the films is studied by X-Ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The surface energy of the films is studied by Water Contact Angle (WCA). The films thickness is determined by profilometry, and the composition of the plasma phase is analyzed by atmospheric Mass Spectrometry (atm-MS) and Optical Emission Spectroscopy (OES).

Results

Very similar atomic composition and surface energies are obtained for the tested range of experimental parameters. Difference in composition, depending on the precursor used, can however be detected in the high resolution C1s peak (XPS). The signature of the precursor can also be detected in the atm-MS results of the plasma phase. OES measurements on the other hand do not allow to easily differentiate the various precursors.

The main species detected other than Ar are F and CF₂. The combination of the gas phase analysis and the films composition suggest a small fragmentation of the monomer in the plasma. Indeed as the initial structure of the precursor can still be detected in the deposited films we can conclude that the chemical structure of the polymerizing species must be close to the one of the initial molecule.

Differences in deposition speed depending on the precursor type and/or the plasma type (AC or DC) are evidenced by profilometry measurements. As expected the precursor containing the unsaturated bond has a higher deposition rate. Thicker films exhibit slightly higher contact angle values (~140°) than thinner ones (~130°). This cannot be attributed to the chemical composition of the films as they are very similar but can be explained by the increased roughness of the thicker samples.

The overall composition of the films can only be slightly modified by changing the precursor structure or the plasma parameters. The deposition speed is the main parameters linked to both the precursors structure and the plasma parameters.

6:00pm **PS+2D-WeA12 Surface Modification of Nafion Membranes Exposed to an atmospheric He-O₂ and He-H₂ Post-Discharge**, *Thierry Dufour, D. Merche, H. Julie, R.F. François*, Université Libre de Bruxelles, Belgium

Nafion is commonly used as a proton-conducting polymer membrane to separate the anode and cathode compartment of proton exchange membrane fuel cells (PEMFC) and water electrolyzers. The use of plasma based technology has contributed to lower catalyst loadings, thus decreasing the production costs. In this framework, our researches have been focused on a simple and robust technique to modify Nafion surface properties, using the post-discharge of an atmospheric RF plasma torch supplied in helium as carrier gas and H₂ or O₂ as reactive gas. The modifications achieved on Nafion samples have been compared with those of common polymers such as polyethylene, PVF and PTFE. Contrarily to these polymers, the Nafion presents more complex etching mechanisms, that may be correlated with the complexity of its molecular formula: (i) its hydrophobic region is a continuous semi-crystalline region which is Teflon®-like, being made up of main chain TFE segments, while (ii) its hydrophilic region (sulfonate group) allows water and proton/ion transport but can also swell and change in size and/or shape with water uptake (eventually forming a continuous network). We have already demonstrated that the chemical nature of the fragment species (ejected from the Nafion film) depends on the exposure time because the fluorinated backbone is not etched as efficiently as the perfluorovinyl ether groups terminated with sulfonate groups.

The morphological and chemical structural changes of the Nafion films during exposure to the post-discharge have been characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) as well as WCA (Water Contact Angle) measurements. Moreover, a characterization of the proton conductivity and of the methanol permeability will also be introduced.

This work is supported by PSI-IAP 7 (plasma surface interactions) from the Belgian Federal Government BELSPO agency.

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