Tuning the electronic and chemical surface properties of graphene combining alkali deposition and low-energy ion irradiation

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ABSTRACT

The presence of defects in graphene due to thin-film processing can lead to alterations of its electronic properties. Tuning of graphene’s electronic properties could be achieved through control of thermal deposition of alkali dopants (e.g. lithium) combined with low-energy deuterium ion irradiation. In this case defect generation may be controlled enhancing tunability. Using X-Ray photoelectron spectroscopy (XPS) the functionality of lithiated polycrystalline graphite and lithiated highly ordered polycrystalline graphite (HOPG) reveal distinct correlations between the fluency of deuterium atoms on the surface. Chemical functionalities of Li-O-D and Li-C-D are observed on the O1s and C1s XPS spectra as deuterium fluency increases. Bulk HOPG and graphite study of deuterium chemical functionality on lithiated graphite lay the foundation elucidating the synergistic effects of doping of lithium and deuterium irradiation have on graphene and hydrogenated graphene (graphane) property tunability.

Keywords: graphene, graphene, alkali metal, ion irradiation, surface chemistry.

1 INTRODUCTION

Single-layer graphene has unique electronic properties with promise for post-silicon nano-electronics [1]. The presence of defects originating from thin-film processing can lead to variation of graphene’s electronic properties in addition to interaction with substrate and environmental conditions. Similar modifications are possible for carbon nanotubes. In particular, the chemical state of the surface plays a major role in the functionality of carbon nanotubes of various geometries (e.g. single-wall carbon nanotubes, few-wall carbon nanotubes, etc...) [2].

Chemical modification can lead to substantial changes in graphene’s or CNT’s electronic properties; such as reversible hydrogenation or alkali adsorption at the graphene or CNT surface [3]. The balance between metallic and covalent bonding in CNTs can also be dramatically influenced by the chemical state at the surface and interface of these materials. Tailoring of graphene’s electronic properties could also, in principle, be achieved by controlled introduction of defects using low-energy ion irradiation [4]. This paper presents unique in-situ measurements that examine the combination of thermal deposition of alkali adsorbates (namely lithium) combined with low-energy deuterium irradiation and its effect on chemical and electronic properties of graphene (hydrogenated graphene) by operating at sub and near-damage threshold ion-beam energy regimes (i.e. E < 100-500 eV/amu). Alkali absorbates have been found to uniquely tailor the electronic band structure of graphene [5]. To elucidate on the fundamental mechanisms that govern alkali-metal interactions with polycrystalline graphite-based systems, experiments depositing lithium coatings on graphite surfaces irradiated with deuterium are conducted. The hydrogen isotope is selected to minimize interference with chemical breakdown of water leading to contributions of hydrogen on the graphitic surface. Lithium is selected as the alkali metal due to its nearly free-electron like electronic properties.

The chemical functionality of lithium with oxygen and carbon in polycrystalline graphite has been recently studied [6,7]. However the chemical functionality and intercalation of lithium in graphene and graphene is undocumented. Furthermore, in-situ surface characterization of lithiated graphitic surface irradiated by D ions on both polycrystalline and highly-oriented pyrolytic graphite is also undocumented. X-ray photoelectron spectroscopy (XPS) results show that the surface chemistry of a Li conditioned graphite sample after D ion bombardment is fundamentally different from that of non-Li conditioned graphite with hydrogenation followed by sp, sp2 and sp3 hybridizations [6]. Instead of simple LiD bonding as seen in pure liquid Li, graphite introduces additional complexities with XPS measuring bonding functionalities between Li-O-D (manifest at 533.0 ± 0.5 eV in the photoelectron spectra) and Li-C-D (manifest at 291.2 ± 0.5 eV) shown in Fig. 1. XPS spectra show Li-O-D and Li-C-D peaks become “saturated” with D at a fluence between 3.8 and 5.2 x 10^{17} cm^{-2}. Controlled experiments indicate D binds to O and C in the presence of Li by means of dipole interactions between Li atoms and the graphite matrix. XPS analysis and TDS (thermal desorption spectroscopy) show that deuterium has at least two bonding states in lithiated graphite: 1) weak bonding due to dipole interaction and 2) covalent bonds to C and O. This paper presents novel in-situ D-irradiation experiments on lithium-treated...
polycrystalline graphite and HOPG surfaces. Data includes in particular the carbon and oxygen states for lithiated graphite as a function of D irradiation dose.

2 EXPERIMENTAL SETUP

The following experiments were performed at OMICRON surface science facility at Birck Nanotechnology Center located at Purdue University. This facility consists of two vacuum chambers, one designated for characterization of samples, and the other for preparation of thermal and energetic particle interactions with material surfaces. The characterization chamber consists of a vacuum in the range of 4.0x10^{-11} Torr. Samples are characterized using X-ray photoelectron spectroscopy (XPS), using an Al K-alpha source (1486.6eV). The preparation chamber is held at 2.0x10^{-9} Torr that includes a Residual Gas Analyzer (RGA) with a quadrupole mass spectrometer (QMS) used for thermal desorption spectroscopy (TDS). Juxtaposed to the sample surface is a quartz crystal microbalance (QCM) that calibrates in-situ the amount of lithium flux from a nearby lithium evaporator. In addition a broad beam ion-beam source that delivers energetic deuterium beams with energies between 250-1000 eV/amu is also used. The beam currents average about 5-10 µA on a 1-cm² area on the sample.

Samples of HOPG and ATJ graphite used for the following experiments consisted of a 1-cm² area. Thermal lithium was evaporated on sample surfaces to a desirable thickness of 2-µm. The thickness was selected based on the known intercalation properties of lithium on graphite. This thickness ensured that an active lithium layer could last through the measurement of the XPS spectra, which ranged from a few minutes to about half an hour. The QCM measured the deposition rate of lithium in Å/s and corresponded to the exposure time of the surface to equate to 2-µm of lithium on the surface. The sample surface was then transferred in vacuum for characterization using XPS. Irradiation with deuterium ions was conducted at an angle of 30-degrees to surface normal and a flux of 2x10^{13} ions cm⁻²s⁻¹. Sequential irradiations were performed and repeated to record XPS spectra at corresponding fluencies of deuterium.

3 RESULTS AND DISCUSSION

3.1 Li intercalation on the surface

Lithium intercalation and chemical functionality in a carbon matrix has been well documented [8,6]. Past work has identified the peak locations and chemical functionalities of XPS spectra for O1s, C1s, and Li 1s binding energies. Literature reports the functionalities of the peak locations in the O1s spectrum to be 530.2 eV relating to Li₂O₂ [9] and the other peak located around 532 eV related to the presence of sub-oxides and hydroxides [10]. Documented XPS spectra yielded a substrate of normal polycrystalline substrate, and didn’t explore the effects on Highly Ordered Polycrystalline Graphite (HOPG).

3.2 Lithium-deuterium interaction on polycrystalline graphite

Deuterium ion bombardment on lithium-treated graphite has been shown using XPS to be fundamentally different than that of non-Li graphite due to hydrogenation followed by sp, sp² and sp³ hybridizations [11]. The interaction of lithium and the graphitic matrix introduces a chemical state whereby when exposed to energetic deuterium, lithium binds they hydrogen isotope via indirect interactions with carbon and oxygen atoms. Moreover, direct interaction of Li and D atoms do occur, however at much higher heats of formation, near 5-6 eV.

Results of deuterium irradiation on 2-µm lithium treated polycrystalline graphite surface are shown in Figs 1 and 2. The data shows the results of multiple XPS scan taken in-situ as a function of D fluence. The resulting data from O1s spectra from Fig 1 shows two dominant peaks located around 533eV and 530eV, the chemical functionality of (Li-O-D) correlates to the 533eV peak position, where the Li₂O₂ remains the chemical functionality of the peak at 530eV. Correlation to the effect of D interactions can be seen as the fluence of D2 ions to the surface is increased. The peak associated with Li-O-D gains relative intensity over the Li₂O₂ as the fluence of D2 ions is increased. This direct relationship between the D2 ions and the relative peak intensity can be further justified when looking into the C1s spectrum in Fig 2.
In the polycrystalline graphite matrix the original C1s spectrum yields a single line at 284.5 eV associated directly with the graphitic peak of carbon. After 2-µm lithium evaporation the graphite peak is still apparent and no new peaks are developed. However after irradiation of the sample with D2 ions a peak at 291eV begins to develop. This peak is not associated with lithium carbonate (292 eV) due to lack of sample exposure to oxygen or atmosphere.

[12]. The 291eV relative intensity begins to increase with D fluence and is eventually saturated and equal to the relative intensity of the graphite peak around 1x10^{17} D+/cm^2.

Figure 2: C1s Spectrum for 2-µm Lithium Evaporated polycrystalline graphite with corresponding D2 fluency. Black = 2x10^{15} D+/cm^2, Red = 1.8x10^{16} D+/cm^2, Blue = 4.0x10^{16} D+/cm^2, Green = 1x10^{17} D+/cm^2.

Such peak parameters as a function of the D2 fluency lead to the chemical functionality of the peak at 291eV and involve Li-C-D interactions. Since the chemical state can depend on surface organization, HOPG experiments were determined critical to these studies. In addition, work on HOPG would be closer to the behavior of graphane.

3.3 Lithium-deuterium interaction on HOPG

A 0.5mm×10mm×10mm sample underwent irradiation conditions identical to the ATJ graphite samples and was exposed to the same fluence of D2 singly-charged ions. Fig 3 and 4 show XPS data from the O1s and C1s regions. Compared to the ATJ graphite peaks spectra there is a slight shift in each of the spectra, 0.5eV, this is due to surface charging on the HOPG samples and the inability to properly ground the sample. These experiments will be repeated in a HR-XPS, monochromic, and charge neutralizing surface science facility in the future.

Figure 3: O1s spectra for 2-µm lithium evaporated HOPG with corresponding D2 fluency. Black= 2.2x10^{15} D+/cm^2, Red = 2x10^{16} D+/cm^2, Blue = 3.6x10^{16} D+/cm^2, Green = 1.1 x10^{17} D+/cm^2

Figure 4: C1s Spectrum for 2-µm lithium evaporated HOPG with corresponding D2 fluency. Black= 2.2x10^{15} D+/cm^2, Red = 2x10^{16} D+/cm^2, Blue = 3.6x10^{16} D+/cm^2, Green = 1.1 x10^{17} D+/cm^2
4 CONCLUSION

The chemical functionality of deuterium to lithium and oxygen yield distinct binding states and associated peak structure from XPS. Both HOPG and polycrystalline graphite samples reveal relative peak intensity from XPS O1s and C1s correlation directly with the fluency of D2 ions. XPS spectrum also relates the chemical saturation of the relative peak intensity’s around $1\times10^{17}$ D/cm². Carbon’s role in the chemical functionality of lithium and deuterium has been observed as well with the depends on D2 irradiation.

5 FUTURE WORK

Modification of not only bulk highly-ordered and polycrystalline graphite, but the functionality of single layer of graphite (graphene) with lithium yields promise for post-silicon nano-electronics. Understanding the change on the electronic and chemical properties of HOPG and graphene need the use of angle-resolved photoelectron spectroscopy (ARPES) coupled to in-situ ultraviolet photoelectron spectroscopy (UPS) and XPS. ARPES can map the electronic band structure of graphane doped with alkali metal (e.g. lithium or potassium) and thus the effect low energy heavy ion irradiations have on graphene electronic properties. Further analysis will identify the irradiation conditions that minimize defect production while tuning the electronic properties of graphene and graphene combined with alkali-metal doping.

REFERENCES