Evidence of Electrochemical Graphene Functionalization by Raman Spectroscopy

Kevin M. Daniels¹, a, *, B. K. Daas¹, N. Srivastava², C. Williams³, R. M. Feenstra², T.S. Sudarshan¹, and MVS Chandrashekhar¹

¹Department of Electrical Engineering, University of South Carolina, Columbia, SC 29208, USA
²Department of Physics, Carnegie Mellon University, Pittsburgh, PA 15213, USA
³Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, USA

¹danielkm@email.sc.edu, *corresponding author

Keywords: Graphene, Electrochemistry, Functionalization, Raman

Abstract. Electrochemical functionalization of epitaxial graphene samples on Si-face 6H-SiC are presented in this work. Three semi-insulating 6H-SiC substrates cut from different boules with varying off cut angle (on axis, 0.5° and 1.0° degrees off axis in the [11-20] direction) were diced into 10mm x 10mm samples and quality epitaxial graphene (EG) grown on top. A home-built electrochemical cell was then used with current applied though a 10% H₂SO₄ solution, with a Pt wire and exposed graphene as the anode and cathode, respectively. Functionalization was determined using Raman spectroscopy and measured by an increase in I(D)/I(G) ratio, increase in fluorescence background and introduction of the C-H bond peak at ~2930 cm⁻¹. Components of the Raman spectra before and after functionalization of all samples used were analyzed to show a substrate dependent effect on functionalization with values such as I(D)/I(G) ratio and normalized fluorescence varying between the substrates.

Introduction

Epitaxial graphene has sparked much interest in the materials and device community, boasting such properties as high electrical conductivity, high thermal conductivity and high tensile strength due to the C-C bond, high room temperature mobility, quasi-ballistic transport of carriers, low noise [1-4] and ability to be produced on large areas on commercial SiC substrates [5]. Epitaxial graphene is produced by thermal desorption of Si from SiC in a vacuum [4] or in argon [6,7]. One of the unique properties of graphene is its zero-bandgap, making it a semi-metal. This zero-gap precludes the fabrication of traditional semiconductor devices due to excessive band-to-band leakage.

However, when hydrogen reacts with the π-bonds of graphene, the delocalized π-electron becomes localized at the C-H bond, decreasing the conductivity, changing the bond hybridization from sp² to sp³ and increasing the C-C bond length ~7% from 1.42Å to 1.52Å [8]. This hydride of graphene is called graphane. The electron localization at the sp³ bond leads to a decrease in conductivity, and opens up a bandgap varying from 0-3.5eV depending on the degree of hydrogenation [8]. This enables new applications in bandgap engineered electronics using carbon-based materials. Furthermore, graphane is as thermodynamically stable as comparable hydrocarbons, more stable than metal hydrides and more stable than graphene by ~0.15eV [8]. To form graphane, graphene must react with hydrogen. While bulk graphite has been observed to be chemically inert, graphene has shown enhanced reactivity with atoms such as fluorine [9] and, most importantly, hydrogen. The extent of the reactivity of graphene was quantified by an increase in the Raman D peak resulting in a higher I(D)/I(G) ratio after functionalization [10].

The difficulty with functionalizing graphene is the need for atomic hydrogen, as hydrogen gas H₂ is unreactive. Techniques implemented by other groups involve in situ development of atomic hydrogen by plasma-assistance [11] or hot filaments [12], as the H-H bond in hydrogen gas requires high energy/temperature to break [11]. With the limitations of current techniques to functionalize...
graphene presented, an alternative, electrochemical means is demonstrated in this paper. Electrochemistry offers the most controlled route to systematic functionalization, as the extent of the hydrogenation of graphene can be precisely controlled by changing the duration of the functionalization. Such control is not as easily achievable using previous techniques. Furthermore, through electrochemistry, reactions can be conducted at ambient conditions, as opposed to the harsh environments in other techniques. The convenience and controllability of electrochemical hydrogenation of graphene therefore provides a more realistic approach for a tunable bandgap in graphene. In this paper, atomic hydrogen is generated through an acidic electrolyte (H$_2$SO$_4$-sulfuric acid), giving free H$^+$ ions that can then be easily attracted to an appropriately biased negative graphene cathode for functionalization.

**Experimental**

Three 6H SiC semi-insulating, on-axis wafers were obtained from II-IV, Inc. for this study. The Si-face was chemical-mechanical polished (CMP). 10 x 10 mm$^2$ samples were diced from these wafers and thoroughly cleaned using a standard RCA clean (TCE, acetone, methanol) and HF to remove any native oxide. Growth of EG was performed by thermal decomposition of a SiC substrate in vacuo [13], <10$^{-5}$ Torr, using an RF furnace. Temperatures for growth ranged from 1250-1450°C, with quality of EG growth verified with atomic force microscopy (AFM) and Raman, showing I(D)/I(G) ratios < 0.2, demonstrating the high quality of the starting material [14,15]. EG layer thicknesses were estimated by x-ray photoelectron spectroscopy, Raman spectroscopy [16] and infrared transmission measurements [17]. For this study only Si-face EG growths were functionalized. EG grown on the non-polar faces of SiC, a and m-plane, which have been shown to have higher I(D)/I(G) ratio than EG grown on polar faces, were used to demonstrate that fluorescence is not a result of large I(D)/I(G) ratio but a result of functionalization.

Atomic hydrogen was generated using a home-built electrochemical setup with current applied through a 10% H$_2$SO$_4$ acid solution. A 99.6% Pt wire and exposed EG (approximately a 4 mm diameter circular area) were used as the anode and cathode, respectively. With this setup, we believe H$^+$ ions in the H$_2$SO$_4$ electrolyte are attracted to the exposed graphene. Oxidation occurs at the Pt anode during this process, and has been investigated and discussed in greater detail elsewhere [18,19]. Thus, in this investigation, we limit ourselves to the reduction of the graphene cathode. Functionalization was confirmed using graphene’s and functionalized graphene’s known Raman peaks [14], and changes in the fluorescence background in the Raman spectra [15].

Raman spectroscopy was performed using a micro-Raman setup with laser excitation wavelength at 632 nm with a spot size of ~2 µm. The Raman system was calibrated using the known Si peak at 520.7 cm$^{-1}$. Reference blank substrate spectra were scaled appropriately and subtracted from the EG spectra to show only the graphene and functionalized graphene peaks [11,15]. All the spectra shown in this paper are difference Raman spectra obtained in this manner. Raman was used as an indication of possible functionalization and reversal by the behavior of the D, G and 2D peaks, which correspond to the disorder-induced peak, in-plane vibrations and double resonant [16], respectively, as well as a C-H bond peak introduced at ~2930 cm$^{-1}$ [12]. The D peak is expected to increase as a function of hydrogenation [10, 11] and further support sp$^3$ hybridization [8, 10, 11].

Substrate dependence was investigated by taking sets of three or more samples from each of the three wafers and functionalizing them using the described experiment. D peak position, the ratio of the D and G peak intensities or I(D)/I(G) ratio, and normalized fluorescence, slope(m)/I(G), where slope(m) is defined as the absolute value of the rate of change of the baseline over the entire Raman spectra before SiC substrate subtraction, were recorded from the pristine EG and functionalized graphene. Samples grown on the a and m planes of SiC, not functionalized, were used to show that the resulting “disorder” shown in the functionalized graphene, which signifies functionalization, was significantly different than that of damaged or nanocrystalline graphite [15].
Results

Fig. 1 shows that the I(D)/I(G) ratio has little effect on the D-peak position in unfuctionalized graphene and non-polar face grown graphene, but functionalized samples are red-shifted with respect to their pristine state, with substantially larger I(D)/I(G) ratios. In Fig. 2, when comparing the D-peak position and the normalized fluorescence slope, the trends in the converted and unconverted graphene are entirely different with much higher slopes seen in the converted samples. Fig. 3 shows a similar trend as Fig. 2, comparing I(D)/I(G) with the normalized fluorescence. As expected, fluorescence is only seen in the functionalized samples as it is only present in hydrocarbons, not in pure carbon. The effects of functionalization are shown to be substrate dependent in Table 1.

![Graph showing D-peak position and I(D)/I(G) ratio](image1)

**Figure 1:** D-peak position compared to the I(D)/I(G) ratio of the Raman spectra of pristine EG, functionalized graphene and nanocrystalline graphene (non-polar face a/m plane growth). Functionalized graphene shows significant red shift in the D-peak position and I(D)/I(G) ratios as high as 2.5.

![Graph showing normalized fluorescence and slope](image2)

**Figure 2:** Normalized fluorescence, slope(m)/I(G) compared to D-peak position of the Raman spectra of pristine EG, functionalized graphene and nanocrystalline graphene (non-polar face a/m plane growth). Increasing normalized fluorescence corresponds with blue-shifting of D-peak position among functionalized graphene. Pristine EG and nanocrystalline normalized fluorescence remain below noise threshold.

![Graph showing normalized fluorescence and I(D)/I(G) ratio](image3)

**Figure 3:** Normalized fluorescence, slope(m)/I(G) compared to I(D)/I(G) ratio of the Raman spectra of pristine EG, functionalized graphene and nanocrystalline graphene (non-polar face a/m plane growth). Increasing I(D)/I(G) ratio matches increasing normalized fluorescence while pristine EG and nanocrystalline remains below the noise threshold.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>D-peak Position Before (cm⁻¹)</th>
<th>D-peak Position After (cm⁻¹)</th>
<th>I(D)/I(G) ratio Before</th>
<th>I(D)/I(G) ratio After</th>
<th>Normalized Fluorescence Before (cm)</th>
<th>Normalized Fluorescence After (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 (1° off)</td>
<td>1348</td>
<td>1330.25</td>
<td>0.21</td>
<td>1.91</td>
<td>3.66x10⁻⁰⁴</td>
<td>1.44x10⁻⁰³</td>
</tr>
<tr>
<td>S12 (on-axis)</td>
<td>1344</td>
<td>1332</td>
<td>0.17</td>
<td>1.32</td>
<td>4.24x10⁻⁰⁴</td>
<td>1.89x10⁻⁰³</td>
</tr>
<tr>
<td>S13 (0.5° off)</td>
<td>1346.5</td>
<td>1327.5</td>
<td>0.13</td>
<td>0.82</td>
<td>3.65x10⁻⁰⁴</td>
<td>4.88x10⁻⁰⁴</td>
</tr>
</tbody>
</table>

Table 1: Average Raman Parameters from Each Substrate before and after Functionalization
Conclusion

An electrochemical process was developed with the purpose of functionalizing graphene grown on SiC substrates. This was done to try to induce a bandgap in the material. Raman spectroscopy was used to characterize the material before and after functionalization. The Raman spectra showed an increase in a sharp D peak, demonstrating possible surface functionalization, introduction of a peak at 2930 cm\(^{-1}\), indicating formation of C-H bonds, and D and 2D peak shifts from pristine EG to functionalized graphene, indicating likely sp\(^3\) hybridization. These claims were distinguished from lattice damage by the presence of the fluorescence background in the functionalized graphene in addition to the lack of fluorescence found in the “disordered” EG grown on a and m-planes of SiC despite having comparably high I(D)/I(G) ratios to functionalized graphene on the Si-face.

By functionalizing samples from three different substrates, substrate dependence was observed based on varying I(D)/I(G) ratios and normalized fluorescence between each substrate with evidence pointing to differences between off-cut angle in the [11-20] direction of SiC as well as variation in off-cut angle in other directions. While evidence of hydrogenation has been shown by Raman, further study is needed to say graphane has been formed.

References
