Raman and X-Ray Photoelectron Spectroscopic Studies of Graphene Devices for Identification of Doping

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Abstract

Tunability of electronic properties of graphene is one of the most promising properties to integrate it to high efficiency devices in the field of electronics. Here we demonstrate the substrate induced doping of CVD graphene devices using polymers with different functional groups. Both X-Ray secondary electron cut off and Raman spectra confirm p-type doping of a PVC-Graphene film when compared to a PMMA-Graphene one. We also systematically analyzed the reversible doping effect of acid-base exposure and UV illumination to further dope the polymer supported graphene devices. The shifts in the Raman 2D band towards lower and then to higher wavenumbers, with sequential exposure to ammonia and hydrochloric acid vapors, suggest n-type doing and restoration of graphene to its original state. Finally, the n-type doping with UV irradiation on half-covered samples was utilized and shown by both XPS and Raman to create two regions with different electronic properties and resistances. These type of controlled and reversible doping routes offer new paths for electronic devices especially towards fabricating graphene p-n junctions.
1. Introduction

Graphene, the two dimensional sp² hybridized hexagonal honeycomb shaped network of pure carbon atoms, has received tremendous interest from researchers due to its unique properties especially in the field of electronics. ¹⁻⁵ This can mostly be attributed to the tunability of electronic properties of graphene. One of the most widely used way for tuning the electronic properties is doping.⁶⁻¹² Graphene doping can be made by electrical, chemical, contact or optical means. In our previous study, we showed that applying a gate voltage, hence creating an electric field, induces free charge carriers on graphene and shifts the Fermi energy, which can be monitored by gate tunable photoemission of XPS peaks.¹³ Contact doping is similar, but in this case electric field is formed due to difference in the work functions of graphene and contact material.¹⁴, ¹⁵ Many others use chemical doping,⁶, ⁸, ¹⁶ which is generally relied on substitution of some of heteroatoms¹⁷⁻¹⁹ to the carbon network or by surface transfer doping.²⁰, ²¹ Although the substitutional doping results in doped and stable graphene, the sp² carbon network is irreversibly disturbed due to defect formation, which also leads to decrease in conductivity and mobility. Chemical doping can also be achieved by exposing the graphene samples to gases or liquids which adsorb on the surface hence cause changes in the Fermi Energy.²² Additionally, ultraviolet irradiation modulated graphene doping is also reported by many others.⁹, ¹¹, ¹², ²³⁻²⁵ Optically driven molecular structure transformation of adsorbed species that cause reversible doping of graphene has recently been reported using pyrene,²⁷ spiropyran,²⁵ and azo-based chromophores.⁹, ¹² Luo et al., showed that a reversible and controlled n-type doping was caused by UV illumination of CVD graphene¹¹ while deep UV illumination under oxygen or ozone environment was reported to induce p-type doping.²³.
Raman spectroscopy is common and well established technique for analysis of graphene and its derivatives. By this method, not only the quality of the layer can be assessed, but also the number of layers of graphene materials can be identified.\textsuperscript{26-28} For graphene, Raman spectra show two main features which are so-called G and 2D bands, and the position of these bands are used to determine the type of doping.\textsuperscript{29, 30} Additionally, presence of D and D’ bands in the Raman spectrum, which are also called defect activated bands, indicative of the changes in the sp\textsuperscript{2} hybridized structure of graphene, have also been used to probe the presence of impurities or defects.\textsuperscript{28, 31, 32}

X-Ray Photoelectron spectroscopy is also frequently used for elemental analysis and also for elucidating the nature of the doped heteroatoms.\textsuperscript{10, 17, 33} In XPS, the sample is irradiated by a known energy of X-rays which results in creation of photoelectrons whose kinetic energies are determined and converted to binding energies using the energy of the X-ray photons and the spectrometer work function. Binding energy of a specific level is different for each atom, which also varies with its chemical environment. Therefore, XPS gives chemical as well as elemental information. XP Survey and high resolution Si2p, C1s and O1s spectra for a typical sample of graphene on SiO\textsubscript{2}/Si substrate are shown in Figure 1. Since XPS is a surface sensitive technique and give information only about the top few nanometers depth of the sample’s surface. Since graphene is a single (or a few) layer of carbon atoms, silicon substrate is within the analysis depth and is observable both in the survey and in the high resolution (in the energy scale) scans. For example, while the Si2p\textsubscript{1/2} peak appears around 100 eV for Si\textsuperscript{0} we also observe a small intensity peak around 104 eV corresponding to the Si\textsuperscript{4+} of the thin native oxide (SiO\textsubscript{2}) layer. In conventional usage, XPS is used to harvest information on; (i) a selected point, (ii) along a line (line-scan), or (iii) on the entire area (areal scan) with a lateral resolution of 30-400 µm. However, in all the data reported in this work, only 100 µm spot and 100 µm
step sizes are used. In line scan or areal modes, since the number of spectra are large, the spectral information is usually condensed and displayed as either; (i) intensity or (ii) binding energy positions of the selected regions, either as intensity or binding energy variations.

![Graphene on silicon wafer with O1s, C1s, and Si2p levels](image)

**Fig. 1.** A Survey XP spectrum of a typical graphene on silicon wafer together with the O1s, C1s and Si2p levels recorded at a higher resolution. O1s and C1s regions consist of a single peak whereas Si2p consists of two peaks assignable to lower binding energy Si^0 and higher binding energy Si^4.

In one alternative use of XPS, application of external bias to the sample is used to cause development of charges on the surface, which allows the user to extract additional electrical properties about the sample, because the position of photoelectron peaks also shifts under the applied potential. For example, the binding energy of Au4f\(_{7/2}\) peak is 84.0 eV, corresponding to the zero oxidation state gold atoms within the metal. When we apply an external bias to the gold substrate the position of photoelectron peak shifts with the same
amplitude of the applied bias due to its excellent conductivity, see Figure 2. However, shifts with different amplitude are usually observed for poorly-conductive or non-conductive materials.

**Fig. 2** (a) Schematic representation of a typical graphene device and behavior of Au4f peaks of the source and the drain electrodes under external bias. (b) 2-Dimensional (areal) contour plot of the Au4f1/2 peak intensity (c) 3-Dimensional plot of the binding energy position of Au4f1/2 within the designated area where x and y axis are distance while the z and color bar both represents the binding energy scale. Data is recorded with 100 µm of X-rays spot size and with 100 µm steps in between two points.

In one of our previous work, we showed that variations in the electrical potential hence the C1s binding energy throughout the sample due to external bias are linearly correlated with the bias applied for a pristine graphene. However, by analysis of peak positions, it was also
demonstrated that the external bias reflects and amplifies the appearance of morphological defects on the graphene layer, see Figure 3.\textsuperscript{35}

![Diagram of graphene with labels indicating external bias and binding energy positions](image)

**Fig. 3** Variations in the C1s binding energy positions of the entire area of the device for; (a) a 330 Ohm pristine graphene sample, and (b) the 4 kOhm oxidized graphene, under +6V external bias to one of the electrodes, while the other is grounded. Their schematic representations are given at the bottom.

As we discussed earlier, XPS is a charge sensitive technique so that the peak positions are also affected and shift due to charging on the surface. This makes XPS a good candidate to analyze doping in theory. However, as we had previously shown that the energy difference between the p-type and n-type Si2p peaks on H terminated Si wafer surfaces is much smaller (0.18 eV) due to band bending, hence it is difficult to fully evaluate the effect of doping, as shown in Figure 4.
Another possibility that photoelectron spectroscopy offers is determination of the work function of the sample through analysis of the low energy cut-off region, dominated by secondary electrons. Such determinations are also used for assessing the type and the extent of doping. The onset of the secondary electron cut-off gives information about the work function of the sample using the relation:

\[
\Phi_{\text{sample}} = h\vartheta - (E_{K,\text{max}} - E_{K,\text{min}})
\]

where \(E_{K,\text{max}}\) is the maximum measured kinetic energy of an electron emitted from the Fermi level, and \(E_{K,\text{min}}\) is the minimum measured kinetic energy which is located in the region of the secondary electron cut-off\(^{36, 37}\). Even though, UPS is generally used for work function determinations due to its higher photon flux\(^{38, 39}\), XPS has also been used in the literature\(^{37, 40, 41}\). However, experimentally it is challenging to measure the electrons with nearly zero kinetic energy using a conventional XPS spectrometer. That is why, generally a negative bias is applied to detect and analyze this region, because the negative bias accelerates the kinetic energy of all electrons to the spectrometer. In our case, to analyze systematically the
secondary cut off region a -30V external bias is applied from the bottom of the silicon wafers. Since this applied bias gives an offset to the entire energy scale in the spectrum, the above equation is still valid. The high resolution Si2p and secondary electron cut-off region are shown in Figure 4 for both an n-type and a p-type H-terminated Si wafers which shows a -0.30 eV difference in the cut-off edge, as opposed to 0.18 eV difference in the Si2p peak.

In this work, by using XPS and Raman Spectroscopy as complementary techniques we investigated substrate induced doping of two polymers with different functional groups on CVD graphene layers. In addition, we used acid and base exposure and also ultraviolet illumination in order to create further doping. Fabrication of a device with two regions, each having a different type of doping, is also demonstrated.

2. Experimental

Device preparation

The graphene used to form devices is produced on a copper foil by chemical vapor deposition at 1035 °C and 10 Torr pressure using flowing methane and hydrogen gases. 2% solutions of PMMA and PVC were prepared in acetone and THF respectively. After the graphene growth, PMMA and PVC solutions are deposited on the graphene side by drop casting. After the coating, polymer layer with graphene and copper is heated to 80 °C and the polymer/graphene film is isolated by dissolving the Cu foil using FeCl₃ solution. Remaining polymer-graphene sample is reverse transferred to the Si wafer, with graphene facing upward. Finally, gold electrodes are deposited on each side of the sample. The process is summarized in Figure 5.
**Fig. 5** Schematic illustration of the device fabrication in the source–drain geometry using the polymer supported graphene and Au electrodes. (a) CVD graphene is prepared on Cu foil. (b) A layer of PMMA (or PVC) is coated on the graphene face through drop casting. (c) Cu foil is etched away using FeCl₃ solution to obtain free-standing Polymer/Graphene films. (d) Polymer-graphene sample is reverse transferred to the Si wafer. (e) Gold electrodes are deposited on each side of the sample.

### Characterization Methods

All XPS measurements are carried out using a Thermo Fisher K-Alpha X-Ray Photoelectron Spectrometer with an energy of 1486.6 eV monochromatic source. The instrument is modified for application of external bias which is controlled by a Keithley 2400 Source-meter. For secondary electron cut-off measurements both electrodes are connected
to the sample holder in order to apply a -30V bias. On the other hand, for the Voltage Contrast XPS measurements one of the electrode is grounded while the external bias is applied to the other one, inducing current flow across the device. Raman spectra are obtained with a Jobin Yvon LABRAM Raman Spectrometer equipped with 532 nm green laser. The laser beam is focused by a 50x objective lens. The scattered radiation is collected by the same objective lens and sent to a CCD detector.

3. Results and Discussion

3.1. Substrate induced effects

Raman spectra for PMMA and PVC supported graphene are shown in Figure 6a. Since the characteristic fingerprints of PVC and PMMA appear in the region below 1500 cm\(^{-1}\) we only focused on the G and 2D peaks coming from the graphene layer where G band is due to Raman active doubly degenerate in plane stretching of sp2 carbons corresponding to E\(_{2g}\) mode and 2D is an overtone of D band which is the in-plane breathing-like mode of carbon rings.\(^{26}\) \(^{28}\) The position of these two features gives information about doping. An upshift of the G band usually demonstrates the occurrence of doping (holes or electrons) in graphene films while the shift in 2D indicates the type of doping. Downshift in 2D band indicates an n-type and upshift indicates a p-type doping.\(^{29}\) \(^{42}\) It is also well-known that, molecules with electron withdrawing groups adsorbed on the surface of graphene will lead to p-type doping of graphene, and molecules with electron donating groups will lead to n-type doping.\[^{[REF]}\] In this case, since both the G and the 2D bands shift to higher wavenumbers, the PVC-Graphene film exhibits p-type shifting compare to the PMMA-Graphene film. As can be seen a shift of \(~11\) cm\(^{-1}\) is observed, which is reproducible.
As was shown in Figure 4 for n- and p-doped Si wafers, the work function is sensitive to the doping level and can be probed by the secondary electron cut-off measurements under -30 V bias. Similar behavior can also be observed for the polymer supported graphene samples, which are now shown in Figure 6b, together with the corresponding shifts detected through Raman measurements shown in Figure 6a. Hence, the secondary electron cut-off measurements also support the more p-type behavior of the graphene on PVC, compared to the graphene on PMMA, which has ~0.6 eV higher cut-off energy. Note also that more than three different samples are prepared and analyzed for ensuring the reproducibility of these findings.

![Graph](image)

Fig. 6 (a) Raman and (b) XP Cut-Off spectra of the PVC/Graphene and the PMMA/Graphene films.

### 3.2. Reversible doping with acid/base exposure

Having demonstrated that the substrates do induce controllable and stable doping on the CVD graphene, we now turn to investigate the effect of exposing the graphene-PVC sample to vapors of acid and base solutions. In this type of doping the exposed molecules are
adsorbed onto the surface and act like acceptors or donors. While a variety of acids and bases have been used in literature, nitric acid is the commonly used one, which is known to reproducibly cause p-type doing on the pristine graphene samples.\textsuperscript{43, 44} However, to our knowledge, doping by acid/base vapors as a further doping/un-doping of the already doped samples has not been reported before. To check the applicability on the graphene samples in the presence of a polymer as a substrate, we sequentially expose the sample to the vapor of ammonia and then hydrochloric acid and record quickly the Raman spectra after each step. Raman spectra of the graphene sample on PVC; (i) as prepared, (ii) after NH\textsubscript{3}, and (iii) HCl exposure are shown in Figure 7b, and the shifts in the G and the 2D bands are depicted in Figure 7c.

Fig. 7 (a) Schematics of the process showing the acid and base vapor exposure steps of PVC/Graphene device (b) Raman spectra of PVC/Graphene as prepared, after NH\textsubscript{3} and then HCl exposure. (c) Shift of Raman 2D band and (d) G band position between treatments for as prepared, after exposure to HCl vapor, and then to NH\textsubscript{3} vapor.
Since the changes in the G band position do not reveal information about the type of the induced doping, it is more informative to evaluate the 2D shifts. Exposing the graphene on PVC to the ammonia vapor causes a blue shift in the spectrum hence indicates induced n-doping which can be reversed back with further exposure to HCl. We also observe that this type of doping is reversible and turns to its original state after a few hours. That is the reason why we do not show the secondary electron cut off spectra using XPS, which is performed under ultra-high vacuum conditions.

3.3. UV irradiation and Voltage Contrast XPS

Although UV irradiation is extensively used to induce doping in different ways in the literature, from our previous studies we know that UV also affects the polymer substrate. For example, in References 45 and 46, we had shown that UV irradiation of PVC causes photo-degradation and releases HCl, i.e. acid vapors, which we also expect to effect the Fermi energy of the graphene overlayer. For this reason, we irradiate only half of both types of polymer supported graphene samples for a duration of 5 hours with UV lamp (mostly 254 nm Hg-Line) by masking the other half. This type of UV irradiation reduces optical transparency of the samples and block the Raman measurement by inducing a saturation in the Raman signal. Therefore, only the secondary electron cut-off measurements under -30V on the UV irradiated and masked region are shown in Figure 8b and 8c for PMMA and PVC supported CVD graphene films, respectively. While the cut off edge clearly shows the n-type doping upon the UV irradiation on PMMA supported sample, there is no measurable shift (hence doping effect) induced by the UV irradiation on the PVC supported one. We believed that the main reason is
the near cancelation of the two opposing effects; (i) n-type doping of the UV, and (ii) p-type doping of the HCl formation during the irradiation.

**Fig. 8 (a)** Schematic representation of UV irradiation on half of the sample together with the Raman spectra of (b) PMMA/Graphene and (c) PVC/Graphene form both the masked and UV-irradiated regions.

For additional information, we recorded the secondary electron cut-off spectra on a line starting from the UV irradiated towards the masked region of the PMMA supported graphene sample, where the clear indication of two regions with different work functions are observed as shown in Figure 9a. Furthermore, we fabricated a device on the same sample by depositing gold electrodes in the source-drain geometry and applied an external bias from one end while the other one is grounded, and acquired spectra on the similar line as in Figure
9a, which are depicted in Figure 9b. This type of measurements is called Voltage Contrast XPS and has extensively been used by our group.\textsuperscript{35} For example, as we showed earlier in Figure 3a that; (i) for the defect free pristine graphene sample the C1s binding energy drop was linear along the line (IR drop), and (ii) in the presence of defects this drop deviated strongly from linearity.\textsuperscript{22} However, very different from the previous findings is that, for the case of half UV irradiated PMMA supported graphene, two different regions with two different slopes are observed, indicating that the two regions have different resistances and carrier concentrations, probed by both the cut-off and also the charge-contrast measurements.

![Diagram]

**Fig. 9** XP spectra of (a) CUT-OFF and (b) C1s regions, recorded in the line scan mode from the one electrode toward the other under -30V gate and +6V source bias respectively.
4. Conclusions

A simple and easy method for doping of CVD-grown graphene is performed with polymers having different functional groups. This method can be applied to any polymer which is not soluble in water. The functional groups of the underlying polymer layer induce doping in the graphene layer. The doping characteristics analyzed for two types of polymer which are PMMA and PVC by Raman Spectroscopy and XPS. This method causes the permanent doping on the graphene layers without introducing further defects. However, by controlled exposure to acid/base vapors or UV one can create regions with different doping types and/or levels in the same film, which might even lead to fabrication of p-n junctions, electrical properties of which can easily be assessed by simple variants of XPS measurements.

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