

P-doped CVD graphene on Si/SiO₂ substrate

Nikos Delikoukos¹, Labrini Sygellou¹, Dimitrios Tasis¹, John Parthenios¹, Costas Galiotis^{1,2} and Konstantinos Papagelis^{1,2}

¹Foundation of Research and Technology Hellas, Institute of Chemical Engineering Sciences, P.O. Box 1414, GR-26504 Patras (Greece)

²Department of Materials Science, University of Patras, GR-26504 Patras (Greece)

nickdelik@upatras.gr

Abstract

Graphene has received much interest due the combination of extremely high mobility of carriers up to $2.5 \times 10^5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and Young's modulus values up to 1 TPa. Such properties make graphene an ideal candidate component in opto-electronic devices. To achieve complete graphene-based electronic circuits, optimization of transfer process to substrates and manipulation of carrier density are prerequisites and of great technological importance. On the other hand, the doping process, which involves controlling charge carrier type and concentration, is a reliable approach to tailor electronic properties of traditional semiconductor materials. Therefore, doping is an indispensable way to intentionally modulate the graphene electron/hole transport properties.

In contrast to traditional semiconductors, the two-dimensional structure of graphene confines the doping process to surface adsorption. Dyes, polymers as well as fused aromatic systems have been used to realize either n-type or p-type doping in the liquid phase [1, 2]. Unfortunately, these reactive molecules may introduce parallel doping effects, due to utilization of liquid media for the doping step. Alternatively, doping can be achieved by means of gas-phase charge transfer in which the secondary doping effects are minimized. Elements such as alkali metals, and halogens show an efficient charge transfer doping effect. Yet, in most cases, they acquire high vacuum conditions for the production of vapors. Apart from these choices, charge transfer doping by gases or volatile liquids has attracted a lot of interest due to their easy control. A variety of substances possess good thermal stability and have very good volatility. Incorporated with the undisturbed basal plane electron conjugation, gas-phase molecular charge transfer doping provides a facile and effective method to dope graphene for future nanoelectronic applications. Recently, numerous reports have appeared in line with this route [3].

In this work, we present the gradual p-type surface doping of chemical vapor deposition (CVD) graphene transferred onto Si/SiO₂ wafers. In this approach, HNO₃ molecules are thermally deposited to form self-assembled charge transfer complexes. The charge transfer mechanism is experimentally interrogated by Raman, X-ray photoelectron (XPS) and Ultraviolet photoemission spectroscopy (UPS) for each doping step. Raman spectroscopy, owing to its sensitivity on the structural and electronic characteristics of graphene, has been proven to be a valuable non-destructive tool to detect, among the others, the doping state of graphene by probing the changes of the so-called G and 2D Raman active bands [4]. The UPS spectra were obtained using HeI irradiation with $h\nu = 21.23 \text{ eV}$ produced by a UV source (model UVS 10/35). The work function (Φ) was determined from the UPS spectra by subtracting their width (i.e. the energy difference between the analyzer Fermi level and the high binding energy cutoff), from the HeI excitation energy. For these measurements a bias of -12.29 V was applied to the sample in order to avoid interference of the spectrometer threshold in the UPS spectra.

In figure 1(left panel) the frequency position and the full width at half maximum (FWHM) of the G band for untreated and doped graphene is presented. As can be clearly inferred from the figure the G band characteristics are position dependent. More specifically, in the pristine sample the mean value of the G peak position (FWHM) appears at 1589.2 cm^{-1} (14.4 cm^{-1}) with a standard deviation of $\pm 1.7 \text{ cm}^{-1}$ ($\pm 2.1 \text{ cm}^{-1}$). After one hour of chemical treatment a significant shift of the mean G-mode frequency takes place occurring at $1593.8 \pm 1.6 \text{ cm}^{-1}$. Also, similar trend follows the FWHM(G) ($11.5 \pm 1.5 \text{ cm}^{-1}$). For two hours of chemical treatment the mean G-mode frequency (FWHM) reaches a value of $1598.7 \pm 2.5 \text{ cm}^{-1}$ ($10.2 \pm 2.8 \text{ cm}^{-1}$). Therefore, the adopted functionalization protocol cause solely charge transfer between graphene and the adsorbed HNO₃ molecules thus modifying the charge density in graphene membrane. The observed hardening of the G-band can be attributed to the shift of the Fermi energy level away from the Dirac points. The work function of undoped transferred graphene and after 2 doping steps was investigated using ultraviolet photoelectron spectroscopy (figure 1 right panel). As shown in the figure after doping the work function increases indicating that the Fermi level shifts closer to the valence band. It should be stressed that at each doping level after the UPS/XPS measurements a red shift of the collected Raman bands towards the corresponding untreated values is observed. This is attributed to

the ultra-high vacuum conditions occurring in the XPS/UPS chamber resulting to a severe desorption of the HNO_3 molecules. Further work avoiding the vacuum conditions of UPS/XPS measurements is in progress in order to reach the maximum level of doping without affecting the structure of graphene. Finally, preliminary Raman data showed that the coverage of the doped samples with a thin PMMA film ($\sim 100\text{nm}$) maintains the doping effect implying an easy method to dope graphene permanently while at the same time keeping its structural integrity.

References

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Figures

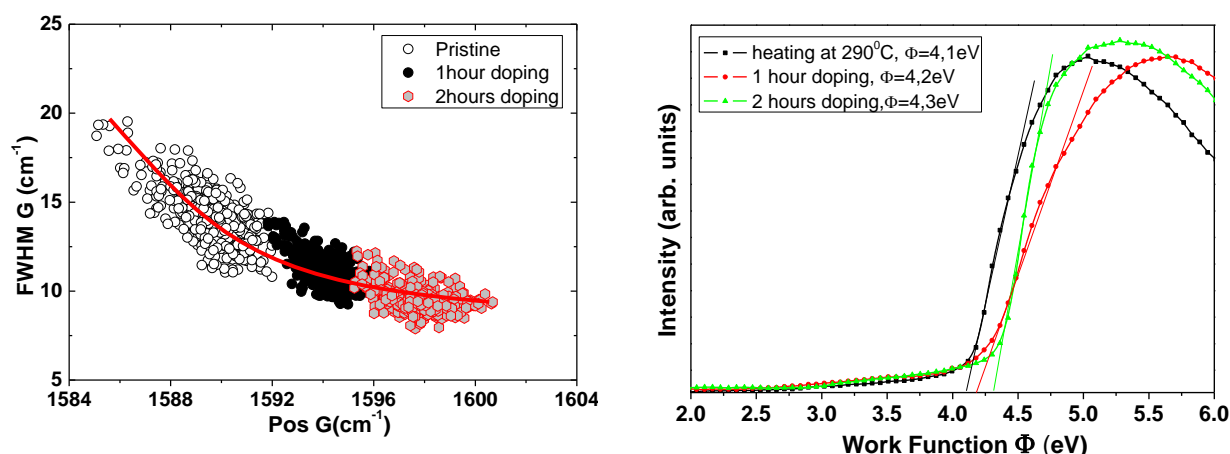


Figure 1. (Left panel) Pos(G) as a function of FWHM(G) for monolayer graphene before and after two doping steps ($\lambda_{\text{exc}} = 514 \text{ nm}$). (Right panel) High binding energy cut-off of the UPS spectra. The curves shown are for transferred graphene on 300nm Si/SiO₂ heated at 290°C for 15min in Ar atmosphere and after two doping levels.