Photoemission Electron Microscopy Investigation of Iodine Doped Graphene

HoKwon Kim1, Anastasia Tyurnina2, Jean-Pierre Simonato2, Jean Dijon2, Denis Rouchon1, Denis Mariolle1, Nicolas Chevalier1, and Olivier Renault1

1 CEA, LETI, Minathec Campus, 38054 Grenoble, France,
2 CEA, LITEN, Minathec Campus, 38054 Grenoble, France.
nokwon.kim@cea.fr

Abstract
Graphene has a great potential in a wide range of electronic applications such as electrochemical cells, photovoltaics, and flexible transparent displays due to its exceptional properties. The large surface area, high charge carrier mobility, exceptional mechanical strength, and chemical stability of graphene make it especially promising as an electrode material. Large scale proof-of-concept devices such as photovoltaic cells, organic electrochemical cells, and supercapacitors have already been demonstrated by high quality large area graphene produced by chemical vapor deposition (CVD) [1] and solution based methods [2]. The current challenge in the area of graphene based electrodes is that intrinsic graphene itself has a low electrical conductivity due to its low density of states at the Fermi level giving sheet resistance as high as ~ 6 kΩ/□ [3]. In order to address this issue, various doping methods have been investigated that can significantly increase the charge carrier concentrations in graphene. One of the common doping methods is the chemical modification of graphene where covalent functionalization by hole/electron donating species such as fluorine, nitrogen, and hydrogen improves the conductivity of the chemically modified graphene [4]. However, this method introduces crystalline defects through the disruption of sp² hexagonal lattice that alter the electronic structure and reduce the carrier mobility values limiting the doping effectiveness. An alternative approach is the attachment of surface adsorbates through physisorption that leads to surface charge transfer between the dopant and graphene. Weakly interacting molecules such as H₂SO₄, HNO₃, HCl, and Br₂ have been investigated as promising candidates for physisorbed dopants [5-7], although the high-temperature and long-term stability of the weakly adsorbed dopants remains an issue [6].

Here, we employ iodine as physisorbed dopants for increasing the hole concentration of graphene produced by CVD method. Iodine has been demonstrated to be a stable and effective dopant for conductive polymers and carbon nanotubes [8, 9]. For graphene, it has been recently shown that iodine can increase the conductivity of single layer graphene film by a factor of 4 [10]. Raman spectroscopy and X-ray Photoelectron Spectroscopy analyses have shown that the doping on graphene is enabled by the formation of anionic charge transfer complexes which mainly consist of I⁻ and I₂⁻ molecules [7]. So far, however, little is known about detailed doping mechanism and the thermal stability of the iodine complexes.

Towards this end, we have employed spectroscopic X-ray photoelectron emission microscopy (XPEEM) on a NanoESCA instrument to analyze at high spatial- and energy resolution the chemical nature of graphene iodine interaction and the effect of in-situ thermal annealing on the transferred CVD graphene 2-probe device on SiO₂/Si substrate (Fig. 1a). The work function mapping measurements performed by UV photoemission threshold spectroscopy and Kelvin force microscopy (KFM) before and after I₂ doping on an heterogeneous area consisting of single (1L) and folded bilayer (2L) graphene domains have shown that iodine can strongly p-dope graphene with a greater effect on the double layer regions (Fig. 1b, c). This is corroborated by I 3d₅/₂ core level imaging of the same area where the double layer has significantly larger concentration of iodine (Fig. 1d). We also confirm the presence I⁻ and I₂⁻ anionic charge transfer complexes via high energy resolution core level spectroscopy for both 1L and 2L graphene.

Further work function and core level analysis of iodine doped graphene immediately followed by in-situ annealing (Fig. 2) has shown that iodine on graphene is stable up to 250 °C where most of iodine is removed at annealing temperature greater than 300 °C, although a significant removal of iodine is observed for 2L graphene starting from 100 °C. Surprisingly, after the complete removal of iodine, the work function of the annealed graphene does not return to that of the graphene sample before the doping treatment. This is ascribed to the residual hydrocarbons due to exposure of the sample in air that appear to act as unintentional n-type dopants in our samples prior to doping [11].

Our work on the doping mechanism and the thermal stability of iodine on graphene provides guidelines for controllably tuning the electronic properties of graphene as well as evaluating potential dopants for graphene based systems for practical applications.
Acknowledgement: The XPEEM and KFM measurements were performed at the Nanocharacterization Platform (PFNC).

References

Figures

![Optical microscope image of transferred graphene film on Si/SiO$_2$ with circular Au electrodes for electrical measurements. Scale bar = 200 μm.](image1)

![Energy-filtered secondary electron PEEM image of the area defined by the green rectangle in a) with regions of 1L, overlapped 2L graphene, Au electrode, and exposed SiO$_2$ substrate.](image2)

![Work function (W. F.) map of the identical region in b). FOV = 98 μm.](image3)

![Integrated I$_3$d 5/2 core level (E$_b$ ~ 619 eV) peak area image on the identical area as Fig. 1 b). FOV = 67 μm.](image4)

![Annealing temperature dependence of work function and iodine concentration for 1L and 2L graphene regions.](image5)