Single-step, Complementary Doping of Graphene

Kevin Brenner and Raghunath Murali[1]
Nanotechnology Research Center, Georgia Institute of Technology

Graphene has recently attracted much interest as an electronic material. With its superior electron transport properties and potential for top down fabrication, graphene could yield truly monolithic systems, with graphene functioning as both the interconnect and switching device. Modern day Complementary Metal-Oxide-Semiconductor (CMOS) technology requires both n and p-type devices to effectively suppress leakage current and power dissipation in static CMOS circuits. Controlled n- and p-type nanoscale doping of graphene is essential to implement post-CMOS circuits and also to obtain enhanced conductivity in graphene interconnects. Graphene exhibits properties that are highly sensitive to interactions with either its edges or basal plane. Significant degrees of doping from the ambient environment, gases, metallization, substrates, and contact with polymers have been observed before in exfoliated graphene.

A variety of doping methods have been previously employed to induce both n and p-type behavior in exfoliated graphene. Room temperature soaks [1] of graphene in dissolved solutions of polyethylene imine and diazonium salts have been shown to induce reversible n and p-type doping, respectively. Edge functionalization [2] of graphene nanoribbons via current anneals in an ammonia environment has been shown to be an effective n-type dopant. Electron-hole asymmetry in graphene devices has been attributed [3] to localized p-type doping of graphene by contact metallization. In addition to this, doping through exposure to aromatic molecules [4] dissolved in solvents has been demonstrated. Reversible doping of graphene via basal-plane bonding with both oxygen [5] and hydrogen [6] has been shown to produce p and n-type behaviors, respectively.

In this work, Hydrogen Silsesquoxane (HSQ) is used to generate a, single-step, complementary doping method for graphene. Due to HSQ's capabilities as a negative tone high-resolution resist, the presented doping method has the potential for highly controlled nanoscale resolution doping over the surface of a chip. HSQ cross-linking has been studied previously [7] and is found to be a complex transition from a hydrogen-rich cage-like structure to a hydrogen-depleted network-like structure. This transition enables the HSQ film to effectively function as both an n-type and p-type dopant. Despite previous reports of doping behavior in graphene, existing methods for the fabrication of p-n junctions are cumbersome, typically involving separate doping steps for p and n regions, and are not suitable for large area fabrication. It is shown here for the first time that a single-step process can be used to induce controllable nanoscale n- and p-type doping across the surface of large area graphene. A p-n junction is demonstrated by using a single lithography step. Mechanisms contributing to this dual-doping of HSQ on graphene will be discussed as well as the controllability offered by e-beam exposure to shift the Fermi level in graphene.

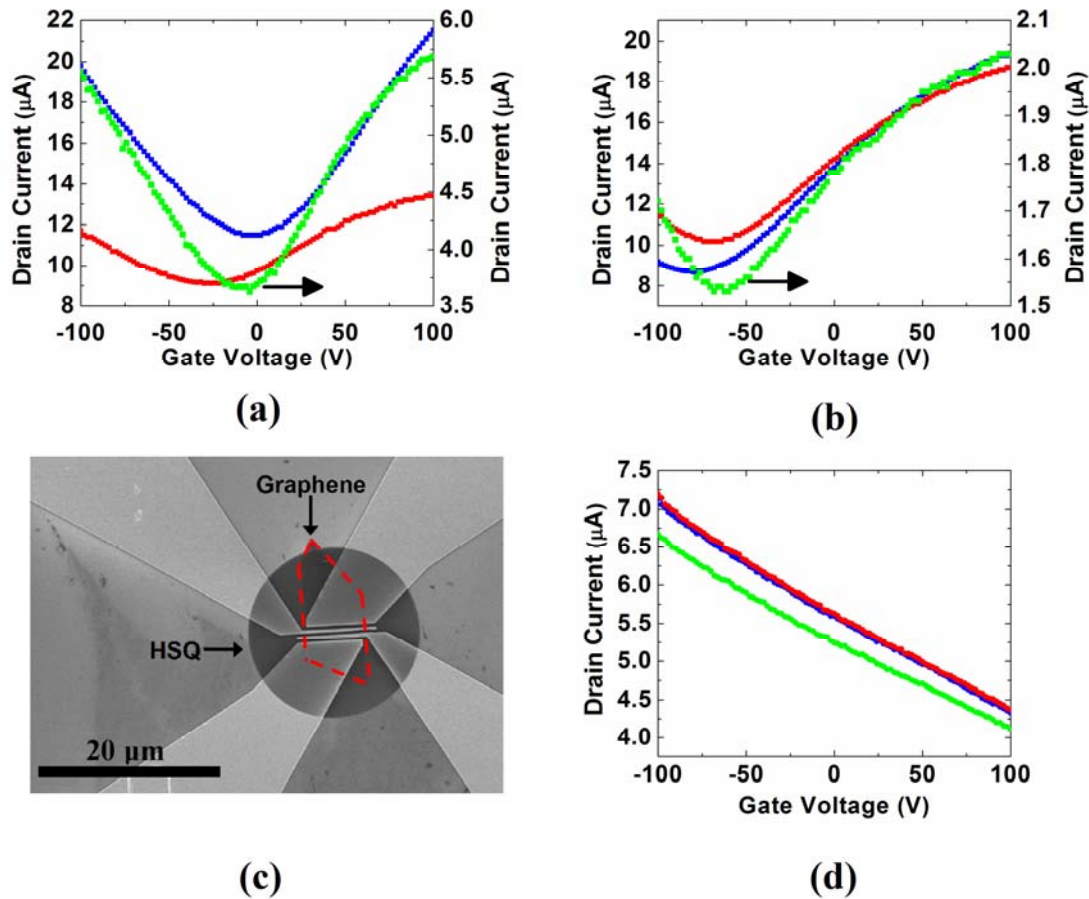
[1] Email: raghu@gatech.edu

Figure: Gated IV curves for three separate devices. (A) I-V curves for three devices after contact metallization. It can be seen that all devices reveal Dirac points residing relatively close to 0 V. This indicates little intrinsic doping in the graphene from initial processing. (B) I-V curves for the same three devices after spinning on 30nm of HSQ, baking, and developing without electron-beam irradiation or plasma exposure. It can be seen from the left shift of the Dirac point that the devices have been strongly n-doped; the same is true when the HSQ film is given low doses. (C) An SEM image of an exposed HSQ pattern over a graphene device. (D) Three separate devices, after exposing an HSQ region (on graphene) with a high dose of 3200 cm^2/V-s. It can be seen that all devices show Dirac points residing beyond 100 V, indicating strong p-doping.

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