Functionalization of Graphene towards Dual-Mode Bio-Sensing

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Abstract

We are developing and investigating an Immunological Ion Sensitive Field Effect Transistor (Im-ISFET) based on graphene grown by CVD and subsequently transferred to desired substrates including transparent foils as in Fig. 1. This Im-ISFET allows us to measure both the current (I-V measurement) through the graphene and the capacitance (C-V measurement) on its surface [1].The measurement setup is schematically shown in Fig. 2. Through C-V measurement, the potential drop over the Electrical Double Layer (EDL) and the capacitance of it are obtained simultaneously. This gives more information about the adsorption of molecules on the graphene surface, and will forward our understanding of the binding of targets to the graphene surface which in turn will give us a deeper understanding of what the measured signals may tell.

Performing C-V measurement with Si-based structures is difficult since a thick oxide layer is necessary to prohibit uncontrolled redox reactions on the surface. This oxide layer has a much smaller capacitance than the EDL capacitance. When measured in series with the EDL capacitance, the oxide capacitance dominates and renders the EDL capacitance undetectable. The use of graphene as the channel material overcomes this challenge. Graphene is much more chemically inert and does not need passivation against electrolytes. A capacitance measurement then only contains two terms: the quantum capacitance of graphene and the EDL capacitance. These two capacitance components are of the same order of magnitude and this enables capacitance measurement of the binding process.

Our focus in this work is on DNA sensing. To make a DNA sensor, it is necessary to bind the DNA probe to the graphene surface via a linker layer. We have employed two different approaches to achieve this layer. One approach is to rely on a self-assembled monolayer (SAM) of an organic molecule 1-pyrenebutanoic acid succinimidyl ester (PYR-NHS)[2]. PYR-NHS has a pyrene group that binds to graphene through pi-pi stacking[3], and a carboxylic group activated by a succinimidyl ester that binds to the probe DNA. The functionalization is done through wet chemistry at room temperature and can be combined with in situ electrical measurements to characterize the coverage of the PYR-NHS. The coverage is also measured by AFM, XPS, SEM, and fluorescence measurement. The fluorescence experiment is carried out by attaching the probe DNA onto a predetermined pattern and then measuring the fluorescence intensity of the labeled target DNA. The selectivity of DNA binding is characterized by measuring the fluorescence intensity on the spots with and without the probe DNA, as seen in Fig. 3. Characterization of the films will also be performed through XPS and SEM.

Another approach is to deposit a thin layer of Au on graphene. The Au layer is so thin that it becomes non-percolating islands spread over the graphene surface. Thiol-based chemistry is then used to attach the DNA probe to the Au. The thiol-chemistry is well established for attaching organic molecules to Au in biochemistry. We have deposited Au layers of different nominal thicknesses by electron-beam evaporation, in order to find a suitable thickness window for sensing. The Au layers are characterized using SEM, grazing incident small angle x-ray scattering (GISAXS) and electrical measurements. An example of the GISAXS measurement is shown in the upper panel of Fig. 4, while the setup and working principle are illustrated in the lower panel of Fig. 4.

References

[1] Chen, S., *et al.*, Applied Physics Letters, **101** (2012) 154106/1-3.
[2] Ohno, Y., *et al*., Journal of the American Chemical Society, **132 (2010)** 18012–3.
[3] Chen, R. J., *et al.*, Journal of the American Chemical Society, **123** (2001) 3838–9.

Figures

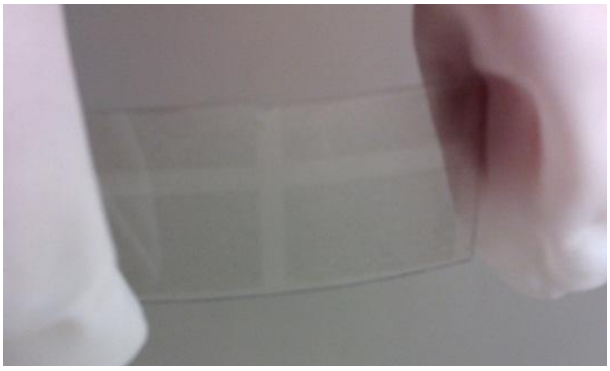

Figure 1: Graphene transferred onto a PET substrate.

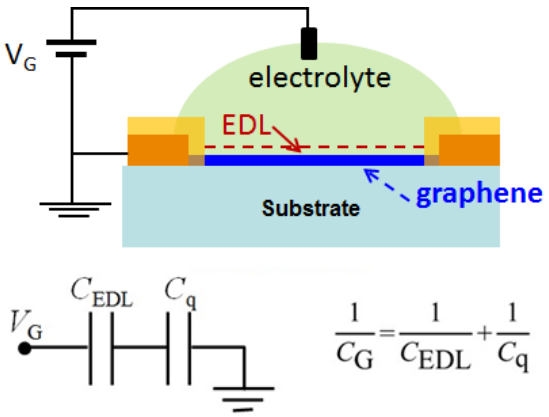

Figure 2: Schematic of the electrical measurement setup as well as the capacitor model with the graphene quantum capacitance C_q and the EDL capacitance C_{EDL} in series.

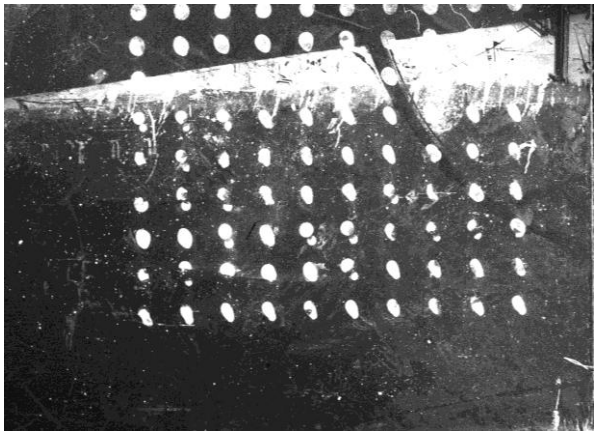

Figure 3: Florescence measurement results with the matrix of round spots representing where the probe DNA has been deposited. The stronger light intensity indicates a higher concentration of target DNA at these spots than anywhere else initially without probe DNA.

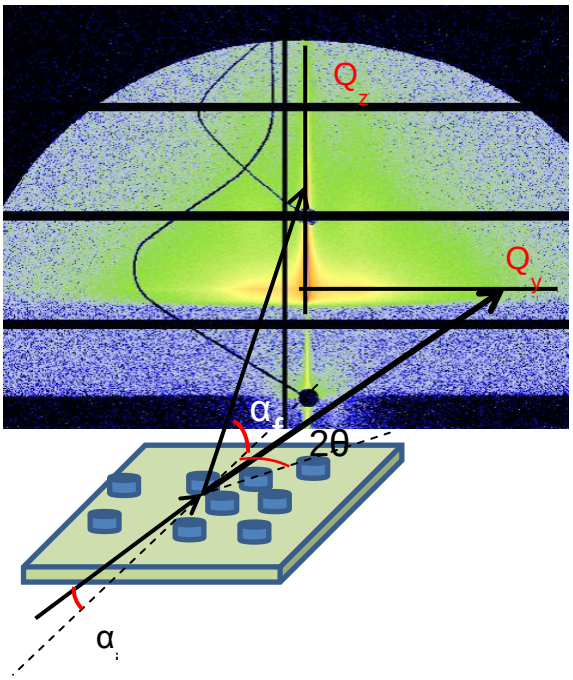

Figure 4: Schematic (lower) of the GISAXS measurement setup and an actual GISAXS image of the sample surface. The intensity and at what output angle the intensity peak is located give information about what kind of layers there are, while the spread out in the y-direction gives information about the lateral structure of the surface.