

Measurement and Manipulation of the Carrier Concentration of Graphene Directly on Conductive Substrates

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The most commonly employed methods to fabricate graphene currently rely on CVD techniques using metal foils as substrate. A problem inherently connected to these growth methods is the fact that graphene is obtained on conductive materials. To be able to use graphene for electronic applications it has to be transferred to an insulating substrate. It has been shown that the transfer process itself (e.g. by wet chemical etching of the metal foil) can strongly degrade the electrical properties of graphene. It would therefore be desirable to have the means to assess the properties of graphene directly on the metal foil without the impact of the transfer procedure.

It is well established that with Raman spectroscopy on graphene one can deduce the desired information by monitoring the shift of the G band caused by an alternation of the carrier concentration [1]. However, this method requires the possibility to change the carrier concentration, which on a highly conductive substrate cannot be performed using conventional solid dielectric based gating techniques and resistance measurements, since the substrate always masks the changes induced in graphene.

In this work we report on a novel measurement approach that allows us to directly study the carrier concentration of graphene on a metal foil. To this end we employ a combination of Raman spectroscopy and solution gating. It has been shown that for epitaxial graphene on SiC, thanks to the transparency of the substrate, graphene can be characterized *in-situ* by illuminating the sample through the substrate [2]. Here, we instead use a dedicated water-dipping objective, which allows us to focus our laser spot by placing the objective directly into the aqueous solution. In our setup we overcome the problem regarding the conductive substrate by taking advantage of the fact that the double layer that builds up at the graphene-solution interface is giving rise to a large electric field only in the vicinity of the interface. The changes induced by charged species accumulating in the solution are screened by the charge carriers in the graphene layer and the metal underneath. Since we are only interested in the surface (e.g. the graphene) we can separate the effects on carbon and on the metal with the use of Raman spectroscopy.

When applying a voltage between a silver wire immersed in the solution and graphene on copper we observe a shift of the Raman G band of about 5 cm^{-1} . This shift is commonly attributed to a change in the electron-phonon coupling strength, which leads to a blue-shift for larger carrier concentrations. We have shown that we are able to initiate changes in carrier concentration even for graphene on metals. By comparing the shift of the G band with literature data for exfoliated graphene [1] we can estimate the change in carrier concentration initiated by our solution gate to be $\sim 1 \cdot 10^{13}\text{ cm}^{-2}$. Our approach can hence be used to optimize the growth for graphene on conductive substrates, since we eliminate the need to transfer the graphene layer for characterization. This allows us to estimate the influence of the transfer process on the transport properties of graphene. The combination of spatial mapping with sub-micrometer resolution together with the possibility to steer the carrier concentration holds great promise to additionally study the influence of grain boundaries on the local electrical properties of graphene.

[1] A. Das et al. *Nature Nanotechnology*, 3, 210 (2008).

[2] J. Binder et al. *Nanotechnology*, 27, 045704 (2016).