Second-Harmonic Generation: a powerful technique for the Visualization of Graphene

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Introduction

Although the first theoretical report on graphene was already published in the 1947 by Wallace [1] the research was boosted by the first observation of an isolated graphene flake by Novoselov and Geim in 2004 [2-3]. Initially, many fascinating physical properties were discovered, such as the extremely high electron and hole mobilities, its intrinsic mechanical strength, the optical transparency and good thermal conductivity, to name a few. Also due to the further development of techniques to synthetize large graphene sheets, nowadays, graphene is a well investigated material in a variety of fields among which are FETs, large scale electronics, flexible electronics, sensors, photonics, energy storage, spintronics ... However, in this work we will further explore the potential of second-harmonic generation (SHG) [4-5-6] imaging as an alternative technique to visualize and characterize graphene structures. The intrinsic surface sensitivity can play an important role in order to characterize the interfaces between stacked layers deposited onto graphene. At this stage, we will benchmark the pristine graphene properties probed by SHG and link them with the widely applied Raman spectroscopy. Additionally, two-photon fluorescence (2PF) images, created by a non-equilibrium electron-hole plasma induced by the ultra-short laserpulses, are recorded [7]. Finally, it is our goal to compare these results with the results obtained from synthetic obtained graphene samples focussing on CVD graphene samples grown on Cu.

Experimental techniques

The exfoliated graphene samples [3] were prepared via standard micromechanical cleavage from graphite and are deposited onto 170 µm thick microscope cover slips. Prior to graphene deposition these glass slides are modified with location markers using standard photolithography. The graphene flakes were firstly screened by optical microscopy. Both the number of layers and the quality of the pristine sample is confirmed by Raman spectroscopy. [8]. A sheet of single layer CVD graphene is transferred from a Cu foil, as obtained from Prof B.J. Cho, KAIST, Korea, grown using their standard techniques as reported in [9-10]. The SHG and 2PF data were recorded by a commercial Zeiss multi-photon microscope (Zeiss LSM 510 META). The fundamental wavelength was 810 nm and the images were recorded with a 10x objective.

Results and discussion

The optical images of the probed samples are represented in figure 1a and 2a, of respectively exfoliated and CVD graphene. By Raman spectroscopy, the number of layers is determined, and in case of the CVD graphene samples the quality of the graphene confirmed. However, in case of the CVD sample we do not have the exact optical image available, but an image of a similar sample is used. Both the SHG and 2PF data are recorded in a region of a uniform sample domain. The inset of the figures shows the images of the SHG (Fig. 1(b) and 2(b)) and 2PF (Fig. 1(c)-2(c)) response. In case of exfoliated graphene, the gradient of intensity overlaps well with the optical image taken, and the signal intensity can additively be linked to the number of graphene layers. In case of the CVD sample area, uniform images are recorded for both SHG and 2PF. The little bright dot in the image can by due to the presence of polymer residuals from the transfer process. Moreover, due to the very high laser powers used, the pristine nature of the graphene flakes cannot be maintained for a long time. However, a clear difference is noted in the sustainability of the graphene flakes towards the illumination time, in which the CVD samples clearly survive longer the imaging process.

Conclusions

In this work we report on the combined SHG and 2PF imaging of the graphene samples, and compare with the results obtained via optical and Raman spectroscopy. We compare the properties of both

exfoliated and CVD graphene, and observe a distinct difference in the laser sustainability for the two graphene types.

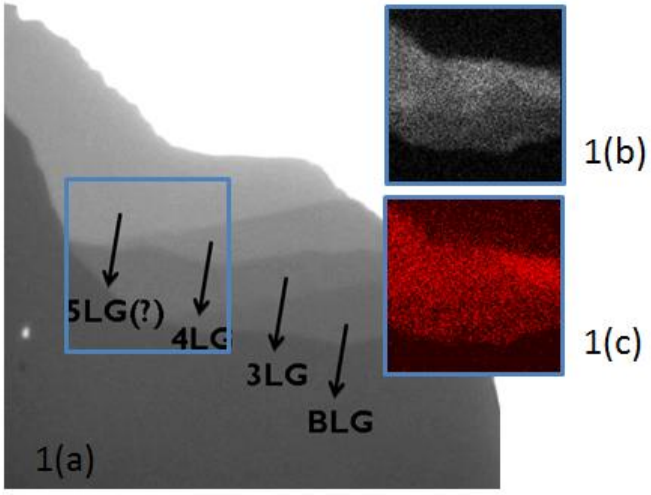

Figure 1: 1(a) optical image of the probed graphene flake, the square demarcates the probed area. 1(b) SHG image 1(c) 2PF image of the same area.

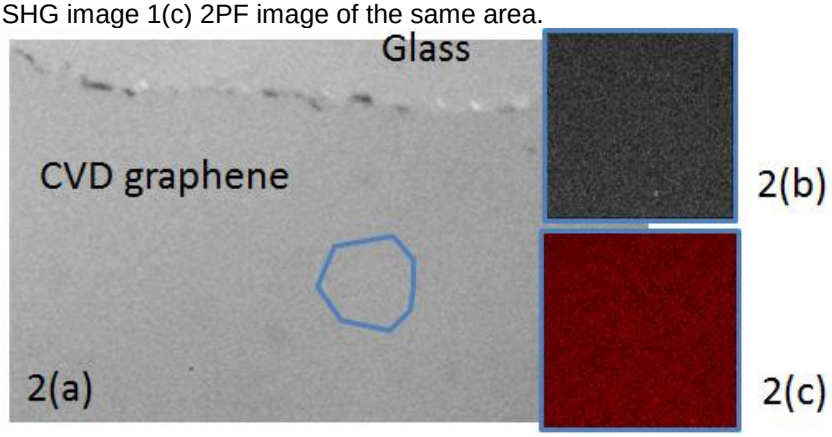

Figure 2: 2(a) optical image of a similar transferred CVD sheet, the line indicates a similar uniform area that is probed. 2(b) SHG image 2(c) 2PF image of the same area as the SHG image is taken.

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