Graphene conductivity mapping using terahertz time-domain reflection spectroscopy

Hungyen Lin[1, 4], Philipp Braeuninger-Weimer[2], Varun S. Kamboj[3], David S. Jessop[3], Riccardo Degl'Innocenti[3], Harvey E. Beere[3], David A. Ritchie[3], Stephan Hofmann[2] and J. Axel Zeitler[4]
[1]Department of Engineering, Lancaster University, Lancaster LA1 4YW, United Kingdom
[2]Department of Engineering, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0FA, UK
[3]Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, UK
[4]Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge CB3 0AS, UK

Abstract—**Graphene conductivity mapping was successfully demonstrated using terahertz time-domain spectroscopy (THz-TDS) operating in transmission geometry. In order to cater for a greater range of substrates and scenarios where transmission geometry becomes prohibitive, here we demonstrate conductivity mapping of large area chemical vapor deposited (CVD) graphene films on sapphire. We validate the technique against measurements performed using the transmission based THz-TDS.**

I. INTRODUCTION

PREVAILING electrical characterization techniques is based on the fabrication of field-effect or Hall bar devices typically combined with Raman spectroscopy. This is time-consuming for large samples and for statistically relevant sample numbers. Among a range of emerging contactless characterization methods, THz-TDS operating in transmission geometry has been demonstrated in order to allow the direct, accurate mapping of graphene conductivity and mobility over large areas, producing data consistent with the Drude model to describe graphene intra-band transitions [1]. Graphene's complex conductivity is determined by the terahertz pulse transmitted through the graphene film relative to the substrate, and analysed using Fresnel coefficients where graphene is modelled as an infinitely thin conducting film. While these demonstrations could potentially enable a rapid in-line graphene monitoring and large-area characterization, to date THz-TDS has only been carried out in transmission mode that necessitates a terahertz transparent support. In this study, we overcome this restriction and demonstrate the quantitative measurement of the electrical conductivity of CVD graphene using THz-TDS operating in reflection geometry.

II. METHODS

Graphene was synthesized using the well-established graphene CVD on commercial copper foil and subsequent poly methyl-methacrylate (PMMA) transfer, which is widely used in literature [2]. Standard copper foils (25 µm thick, Alfa Aesar purity 99.8%) and CH4 as the carbon precursor [3]. For transfer, PMMA was used as support, followed by FeCl3 chemical etching to remove the copper. As target substrate we used sapphire (430 µm thick). Raman spectroscopy was performed using a 532 nm laser for characterizing the transferred graphene. Transferred graphene on sapphire was measured with a Terahertz Pulsed Imaging (TPI) Imaga 2000 system (TeraView, Cambridge, UK) at a step size of 200 µm, where 15 waveform traces were averaged to represent a measurement for one single pixel. One of the main barriers for accurately extracting optical parameters in reflection geometry is the great sensitivity to any phase misalignment between the sample and reference measurements. Attention was given to precise sample positioning by having both the reference mirror and the sample mounted on a motorised stage and positioning the respective front surfaces in order to ensure that the particular reflecting plane reflects the incident wave into the detector at maximum level. It should also be noted that the substrate refractive index measured is not adversely affected by phase misalignment, as in the case for the extinction coefficient [4]. As an experimental check, the measured substrate refractive index for s-polarisation was always compared against the literature values. The reflection coefficient depends on the polarisation of the incident terahertz wave and the angle of incidence. Given the substrate refractive index and using Tinkham's formulae to describe the effect of a thin conducting film [5], the equation for obtaining conductivity from s-polarisation reflection measurements can be derived as

$$\tilde{\sigma} = \frac{\tilde{n}_1 cos\theta_i(1-\tilde{r}) - (1+\tilde{r})\sqrt{\tilde{n}_2^2 - sin^2\theta_i}}{z_0(1+\tilde{r})}$$

where $\tilde{r}$ is the Fourier transformed ratio of the reflected wave's complex electric field from the sample to the incident wave from the mirror, z_0 is the vacuum impedance (376.7 Ω), θ_i and θ_t are the incident and transmitted angles, respectively, and $\tilde{n}_1$ and $\tilde{n}_2$ are the complex refractive indices of air and substrate, respectively [6]. As conductivity spectra has a slope value close to zero, our phase correction method shifts the acquired reflection pulse with respect to the reference measurement in the time-domain so that the real part of the calculated conductivity spectra also has a slope close to zero. For validation of the measurements, the same graphene on sapphire was scanned with THz-TDS operating in transmission mode (Tera K15 T-Light, Menlo Systems GmbH, Germany) with a beam diameter of approximately 1 mm at 1 THz and performed analysis as detailed in [1].

III. RESULTS

In a manner similar to the literature [1, 7] and as shown in Fig. 1, the graphene conductivity spectra on sapphire for our measurement does have a real part characterised by a flat spectral response near to its DC value well below the Drude roll-off frequency while the imaginary part is close to zero [8]. Figure 2a-c shows the Raman graphene D/G ratio map, frequency distribution, and 2D/G ratio map of the transferred graphene on sapphire. Most measured points show a D/G ratio of roughly 10%, highlighting the presence of defects that were introduced during the transfer procedure. The 2D/G ratio map shows an average value of more than one highlighting that the film is predominately monolayer graphene. Figure 2 compares the conductivity map and histogram obtained with terahertz transmission and reflection mode TDS, respectively. The conductivity map acquired in reflection mode contains intermittent interlacing artefacts between alternate rows on the image due to the small signal fluctuations that propagate to the conductivity calculation. When comparing the histogram in Figure 2g, the conductivity frequency distribution generally agrees despite differences in the terahertz spot sizes. For a fair comparison, spatial filtering was applied to the reflection conductivity map to emulate a spot size approximately 2.4 times greater in order to generate a spatially averaged conductivity map and histogram shown in figures 1f and h, respectively. This results show a much closer agreement against the transmission measurements [8].

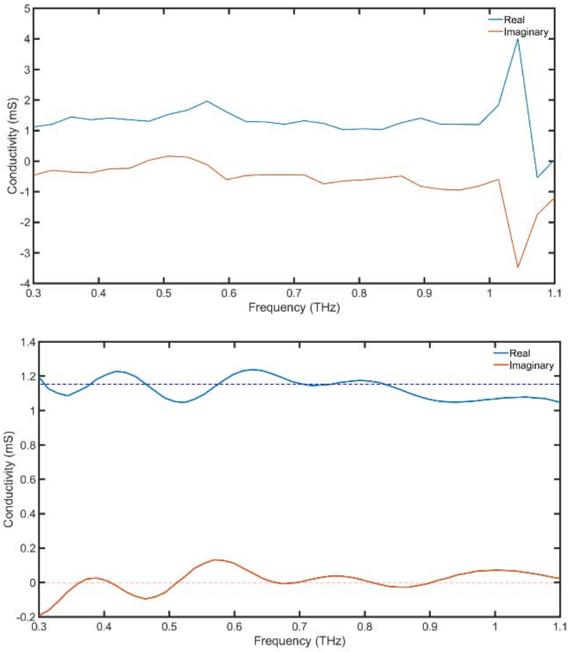

Fig. 1. Graphene's complex conductivity spectra on sapphire measured using THz-TDS operating in the transmission (top) and reflection geometry (bottom).

IV. SUMMARY

We have demonstrated the feasibility and potential of measuring the electrical conductivity of CVD graphene with THz-TDS in reflection geometry. Using terahertz transparent sapphire support, we have validated the technique against current state-of-the-art THz-TDS transmission measurements, where after taking into account the differences in terahertz spot sizes, we find a close agreement between the conductivity histograms.

ACKNOWLEDGEMENT

H.L. and J.A.Z. acknowledge financial support from the EPSRC (Grant No. EP/L019922/1 and EP/R019460/1). P.B.W. acknowledges EPSRC Cambridge NanoDTC EP/G037221/1. R.D., H.E.B. and D. R. acknowledge financial support from the EPSRC (Grant No. EP/J017671/1, Coherent Terahertz Systems). S.H. acknowledges funding from the EPSRC (Grant No. EP/K016636/1, GRAPHTED). H.L. and P.B.W also thank Dr Patrick Whelan for useful discussion.

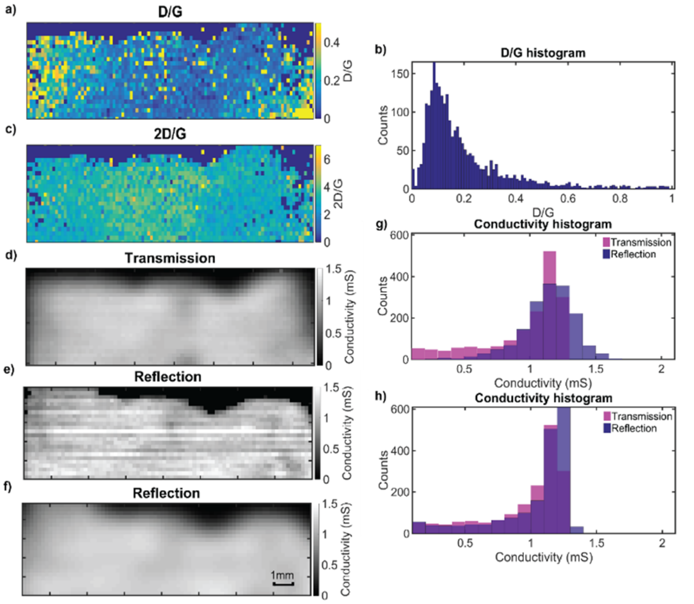

Fig. 2. Raman map of graphene on sapphire substrate, a) D/G ratio map, b) D/G frequency distribution, c) Raman 2D/G map. For the same region a conductivity map of graphene on sapphire substrate was measured with THz-TDS between 0.6-0.9 THz operating in d) transmission mode and e) in reflection mode, where f) shows a spatially filtered map of e) with a spot size 2.4 times greater. Conductivity histograms for transmission and reflection geometries are compared in g) before and h) after filtering.

REFERENCES

[1]. J. D. Buron et al., "Graphene conductance uniformity mapping," Nano Letters, vol. 12, 5074-5081, 2012.

[2] A. Reina et al. "Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition," Nano Letters vol. 9, 30–35, 2009.

[3] P. Braeuninger-Weimer et al., "Understanding and Controlling Cu-Catalyzed Graphene Nucleation: The Role of Impurities, Roughness, and Oxygen Scavenging," Chemistry of Materials, vol. 28, 8905–8915, 2016.

[4] T. Nagashima, and M. Hangyo, "Measurement of complex optical constants of a highly doped Si wafer using terahertz ellipsometry." Applied Physics Letters, vol. 79, 3917–3919, 2001.

[5] M. Tinkham, "Energy Gap Interpretation of Experiments on Infrared Transmission through Superconducting Films," Phys Rev, vol. 104, 845–846, 1956.

[6] M. Thoman et al., "Nanostructured gold films as broadband terahertz antireflection coatings," Phys Rev B, vol 77, 195405, 2008.

[7] J. L. Tomaino et al. "Terahertz imaging and spectroscopy of large-area single-layer graphene", Opt Express, vol. 19, 141–146, 2011.

[8]. H. Lin et al.," Contactless graphene conductivity mapping on a wide range of substrates with terahertz time-domain reflection spectroscopy," Sci. Rep., vol. 7, 10625, 2017.