# Through-substrate terahertz time-domain reflection spectroscopy for environmental graphene conductivity mapping

Hungyen Lin[1, a)], Oliver J. Burton[2], Sebastian Engelbrecht[3], Kai-Henning Tybussek[3], Bernd M. Fischer[3], and Stephan Hofmann[2]

[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, United Kingdom*

[3]*French-German Research Institute of Saint-Louis, Saint-Louis, 68301, France*

We demonstrate how terahertz time-domain spectroscopy (THz-TDS) operating in reflection geometry can be used for quantitative conductivity mapping of large area chemical vapour deposited graphene films through silicon support. We validate the technique against measurements performed using the established transmission based THz-TDS. Our through-substrate approach allows unhindered access to the graphene top surface, and thus, as we discuss, opens up pathways to perform in-situ and in-operando THz-TDS using environmental cells.

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a) Author to whom correspondence should be addressed. h.lin2@lancaster.ac.uk

Significant progress has been made in the crystal growth of 2D materials, particularly for graphene where large-area, highly crystalline mono-layer films can now routinely be produced by chemical vapour deposition (CVD) [1-5]. For scaled graphene manufacturing and many emerging device applications, often not growth itself but adequate characterisation and quality control of the graphene films has become the key challenge [6, 7] . Among a range of emerging contactless electrical characterisation methods [6], terahertz time-domain spectroscopy (THz-TDS) operating in transmission geometry has demonstrated to accurately map the conductivity and mobility of graphene over large areas, producing data consistent with the Drude model to describe graphene intra-band transitions [8-13]. Graphene's complex conductivity is determined by the THz pulse transmitted through the graphene film relative to the support, and analysed using Fresnel coefficients where graphene is modelled as an infinitely thin conducting film. Drift and field-effect mobilities can then be extracted by fitting the conductivity spectra to Drude model [14], and measuring conductivity changes in response to back-gate voltages [15], respectively. By repeating the measurement and analysis across the entire graphene area, a conductivity or mobility map can be reliably produced. Measurements have since been extended to reflection geometry [16, 17] because 1) limited power can be generated with currently available pulsed THz sources; 2) scenarios that prohibit a direct line-of-sight measurement.

In this letter we demonstrate reflection-based THz-TDS of graphene through the supporting substrate. We show that this approach allows us to keep the previously established contactless mapping capabilities, while giving unhindered access to the graphene top surface, and thus, opening up pathways to perform in-situ and in-operando THz-TDS using environmental cells. We employ Si wafers not only as support for CVD graphene films but simultaneously as window to an environmental cell and, as proof of principle, show that graphene conductivity changes based on different gas environments can be straightforwardly measured by this approach. We validate the technique against current state-of-the-art THz-TDS transmission measurements and demonstrate close agreement between the conductivity histograms for different graphene samples. We discuss the many future possibilities that this approach opens ranging from gas- and biosensor development to fast, non-contact, wafer scale correlative probing combined for instance with imaging ellipsometry [18].

As reference process and material, we use well-established graphene CVD on commercial Cu foil and subsequent PMMA (poly methyl-methacrylate) transfer [19, 20] and for which we developed well calibrated processes [2, 3]. We use standard Cu foils (25 µm thick, Alfa Aesar purity 99.8%) and $CH_4$ as the carbon precursor [2]. For transfer, PMMA was used as support, followed by $(NH_4)_2S_2O_8$ chemical etching to remove the Cu. As target substrate, we used float-zone Si wafers (1000 ± 25 µm thick) because of low dispersion and absorption properties in the far-infrared range [21]. Raman spectroscopy was performed using a 532 nm laser for characterising the transferred graphene.

Reflection-based THz-TDS experiments were conducted with a TeraFlash system (Toptica, Munich, Germany), shown in Figure 1. The THz radiation used here is broadband, covering a spectral range of 0.15–3 THz in free-space, and is generated by pumping a biased photoconductive antenna with an ultrashort laser pulse from a femtosecond laser operating at 1560 nm. The emitted THz pulse is collected, collimated by a parabolic mirror of 101.16 mm focal length where a portion of the generated THz pulse is transmitted through a 3 mm thick high resistivity silicon wafer, which functions as a beam-splitter, and is focussed onto the sample at normal incidence by another parabolic mirror. The reflected pulse is then partly reflected by the silicon wafer and detected by the detector via a third parabolic mirror. Such a reflection system achieves a THz beam diameter of approximately 1.2 mm at 1 THz. One of the main barriers for accurately extracting optical parameters in reflection is the sensitivity to phase misalignment between the sample and reference measurements. This requirement is mitigated by using first (air-substrate) and second (substrate-graphene-air) reflections as reference and sample signals, respectively [22]. Given the substrate refractive index and Tinkham's formulae for thin conducting film [23], the equation for obtaining complex conductivity from the reflection measurements at normal incidence in free-space using plane-wave approximation can be derived as

$$\tilde{\sigma} = \frac{(n_s(A^2-1)+A^2+2Acos\emptyset+1)-j(2An_ssin\emptyset)}{z_0(1+A^2+2Acos\emptyset)} \tag{1}$$

where $Ae^{j\emptyset} = \frac{\tilde{r}\rho_{as}\exp(\frac{j2n_s\omega l}{c})}{\tau_{as}\tau_{sa}}$ with $\tilde{r}$ being the Fourier transformed ratio between the reflected wave's complex electric field from the sample to the reference of refractive index $n_s$ and thickness $l$. Other parameters such as $\rho_{as}$, $\tau_{as}$ and $\tau_{sa}$ correspond to Fresnel's reflection $\rho$ and transmission $\tau$ coefficients where the subscripts indicate the dielectric interfaces: air (a), substrate (s). $\omega$ is the angular frequency, $c$ is the speed of light in vacuum and $z_0$ is the vacuum impedance (376.7 Ω). The use of plane-wave approximation is valid in Eqn. 1 because of a relatively low numerical aperture (~0.25). Such approximations were also used for analysing transmission measurements [8, 24], which have been validated using micro four-point probe measurements [8]. Analytical simulation was then performed to validate the derived expression and additionally provided a means to investigate the effect of varying substrate thickness (several microns) on the graphene's complex conductivity spectra [16], which can then be corrected by iteratively multiplying a phase shift term $\exp(\frac{j2n_s\omega\Delta x}{c})$, where $\Delta x$ corresponds to thickness variation. Similar phase compensation scheme was also demonstrated for transmission [13]. Graphene on silicon substrate was measured with the THz spectrometer in Fig. 1 at a step size of 500 μm where 50 waveforms were averaged to represent a measurement for a single pixel under nitrogen purge. As the first reflection was well separated from the second reflection, a time windowing function was used to isolate the acquired waveforms. A spatially-averaged conductivity map was subsequently generated by raster scanning the sample and performing the analysis using Eqn. 1. In order to validate our proposed method, the same sample was scanned using a THz spectrometer configured in transmission geometry with four off-axis parabolic mirrors. The sample at normal incidence to the incident THz beam was placed at the focus point between two central parabolic mirrors also under nitrogen purge. Data were also acquired at

50 waveforms averages at 500 μm step sizes. By performing the analysis detailed in [8, 24], a spatially-averaged conductivity map for approximately the same area was generated.

Figure 2 a-d) shows THz reflections from the graphene sample, with maps showing the primary and secondary peak intensities and waveforms from points on substrate and graphene. The corresponding Raman 2D/G ratio map (see Fig. S1a-c) shows an average 2D/G ratio of around 4 highlighting that the film is predominately monolayer graphene. As expected, graphene covered areas correspond to regions with attenuated reflected THz intensities relative to the support due to a higher carrier absorption [24]. With the support being sufficiently thick, a series of reflected THz pulses are separated out in the time-domain (Fig. 2c) where the first and second reflections are used as the reference and sample, respectively. The measured refractive index is 3.2 in close agreement with 3.29 measured using transmission THz-TDS, which is within 5% of the literature value [21]. The slight discrepancy may be due to sample surface related imperfections, leading to scattering losses and measurement using a focused beam as opposed to a collimated beam [25]. These values are then used to calculate graphene's complex conductivity spectra shown using Eqn. 1 without any phase correction, where a flat conductivity spectrum can be observed. This spectrum is compared against the conductivity spectrum measured using transmission THz-TDS at a similar graphene location. The small peaks in the reflection spectra at 0.55 THz and 0.75 THz are artefacts caused by water line absorption in ambient air inside the nitrogen purged environment due a slightly longer THz beam-path with a possibly lower nitrogen flow than the transmission environment. As any phase misalignment would only significantly affect the imaginary part of the conductivity [13], we place our emphasis only on the real part of the conductivity. As the conductivity spectrum are approximately constant over the spectral range, the representative conductivity is taken as the average between 0.8 to 1 THz to avoid the water absorption lines without substantial loss to spatial resolution. Figure 3 compares the conductivity map and Gaussian-fitted histogram obtained using the transmission THz-TDS and the proposed method, where a good agreement between the averages of the two measurements can be seen

($\sigma_{trans} = 0.57\ mS, \sigma_{refl} = 0.60\ mS$). As an additional validation, the proposed technique at a reduced spatial resolution was applied to a defective sample with two scratches, to generate conductivity maps between 0.5 to 1 THz (due to an absence of distinct water lines in Fig. S2), where a good agreement between the averages of the two measurements is also observed ($\sigma_{trans} = 0.69\ mS, \sigma_{refl} = 0.65\ mS$). The demonstration of the through-substrate reflection measurement means that conductivity can be reasonably estimated directly from the first transmitted or reflected pulse, as previously demonstrated [13, 16], even if the pulse has already undergone a longer propagation path and through the supporting substrate on a system with reduced bandwidth and signal intensity (only a maximum 15% of signal intensity will arrive at the detector for a mirror reflection in Fig. 1). Compared to transmission measurements where spatial resolutions are typically in the order of several hundreds of microns [8, 24], achieving a comparable or higher spatial resolution through-substrate is more difficult because the beam will refract towards the surface normal at a medium of higher refractive index. The frequency dependent THz beam diameter can be estimated from the focal length of the off-axis mirror and the collimated beam size using Gaussian optics [26], but this estimate is only reliable if the Rayleigh range of the focusing mirror is greater than substrate thickness [27, 28].

As the local environment can easily modulate graphene's intrinsic electrical properties upon adsorption, here we demonstrate the potential of the proposed method for resolving conductivity changes induced by ambient conditions. In particular, we performed a measurement without nitrogen purge at a laboratory controlled relative humidity level of approximately 30 to 40%. The reasons for doing so without a designated environmental cell inside a nitrogen purge environment are: 1) it is widely known that polar gases resonate at discrete frequencies in the microwave to infrared spectral ranges leading to sharp resonances corresponding to the transitions between rotational quantum levels, characteristic to the molecular structure [29]; 2) the main constituents of ambient air are nitrogen, oxygen and water vapour; 3) remaining polar constituents in the ambient air are observed to have negligible effect on the THz spectra in the experimental setting (see Fig. S3). Figure 4 compares the complex conductivity spectra of graphene acquired under a nitrogen purge and ambient conditions. As expected, artefacts from the water vapour absorption lines become more pronounced in an ambient condition relative to the nitrogen environment. To quantify the average conductivity change, a representative conductivity is taken as the average between 0.3 to 0.9 THz excluding water vapour line resonances at spectral ranges of 0.5 to 0.6 THz and 0.7 to 0.83 THz. The choice to extend the bandwidth from previously is to ensure a greater number of data points can be included as part of averaging especially after water vapour line resonances are excluded. These excluded spectral ranges were selected to be sufficiently broad in case of water line broadening in the unlikely event of pressure or temperature change. By aggregating conductivity values across the graphene covered areas, the corresponding histogram is generated and compared against the nitrogen purged data. The conductivity averages are then obtained by Gaussian curve-fitting the histograms for the graphene area excluding boundary pixels using the least absolute residual method, resulting in mean values of 0.68 and 0.666 mS for ambient and nitrogen environment, respectively on one day, and mean values of 0.72 and 0.68 mS on another day. This small 2 to 5% conductivity increase is at the same order of magnitude but slightly higher than what was reported in an earlier work using direct electrical measurement on a 44 x 80 μm patch of CVD graphene on $SiO_2$/Si wafer support [30]. The slightly higher conductivity reading can be attributed to several factors, such as probing a significantly larger graphene area (at least four orders of magnitude greater) and performing the measurement without a designated environmental cell thus needing to exclude water vapour contributions. At such a small conductivity change, one also needs to be aware of system's uncertainties, which can be analysed by comparing the two acquired nitrogen averages resulting in an estimate of 2%. However, this number is likely to be an over-estimate as it assumes a perfect, reproducible nitrogen purge in the two days, which in practice is difficult to realise thus resulting in unintentional doping from other moieties in the ambient air [31]. The fact that the conductivity change is close to previous work [30] is promising and suggests a method of performing in-situ and in-operando

THz-TDS of graphene films inside environmental cells as graphene's electrical conductivity is being modified by the local environment [31, 32]. In constructing the cells, even though Si support has been demonstrated, other materials can also be used provided that they have low dispersion and absorption at THz frequencies [16, 21]. Further, the support should be thick enough, with well-polished interfaces, to allow the reflected THz pulses to be well separated in the time-domain for temporal windowing. Finally, the medium immersing graphene should satisfy the semi-infinite slab assumption such that subsequent reflections are minimised resulting in no interference with the medium-graphene-substrate reflection. The immersion medium could be an optically dense dielectric or a thick sample, because an optically dense media, such as liquid water, will absorb almost all incident THz radiation, while a thick sample will provide sufficient delay for subsequent windowing. By being able to gain an unhindered access to the graphene film, our proposed approach can also be combined with imaging ellipsometry [18], which could measure graphene directly from an opposing side to the incident THz wave, as part of correlative probe in order to simultaneously map out electrical conductivity and structural information (layer number, defects and contamination) at different length scales.

In summary, we have demonstrated the feasibility and potential of measuring the electrical conductivity of CVD graphene through the supporting substrate using THz-TDS in reflection geometry, where the supporting substrate can simultaneously function as viewing window to an environment designed to modify graphene's electrical properties. Using a THz transparent silicon support, we have validated the proposed technique against a direct measurement using state-of-the-art THz-TDS transmission measurements where there is close agreement between the conductivity histograms for two samples. We have further demonstrated the sensitivity of the technique to resolve conductivity changes induced by the ambient conditions relative to a nitrogen purged environment, where the resolved changes across large-area graphene is consistent with standard electrical measurements. Our proposed technique opens up the possibility to measure the electrical conductivity of graphene in-situ without any physical contact, underpinning future continuous macroscopic conductivity monitoring and opening up pathways to perform in-situ and in-operando THz-TDS using environmental cells. The unhindered nature of the measurement can additionally be used as part of correlative probing to yield simultaneous electrical and structural information.

## Supplementary Material

See supplementary material for Raman map, conductivity spectra of the defective sample and magnitude spectrum of silicon reflection in ambient and nitrogen environment.

## Acknowledgments

H.L. acknowledge financial support from the EPSRC (Grant No. EP/R019460/1). S.H. acknowledges funding from the EPSRC (Grant No. EP/K016636/1, GRAPHTED). H.L. and O.B. also thank Dr Philipp Braeuninger-Weimer for useful discussion. Additional data for this article is available at https://doi.org/10.17635/lancaster/researchdata/336.

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## Figure captions

FIG. 1. Schematic of the reflection-based THz-TDS to measure the complex conductivity of graphene through the substrate inside a nitrogen purge environment

FIG. 2. Primary a) and secondary b) peak THz intensity maps measured using THz-TDS in reflection geometry through the substrate. The corresponding THz reflection on the substrate and graphene in c) in order to calculate the graphene's conductivity spectra for comparison against transmission d).

FIG. 3. Conductivity maps of graphene on silicon measured directly using transmission THz-TDS in a) and d), and through the substrate in reflection in b) and e). The respective conductivity histograms are compared in c) and f) with darkened colour representing overlap between the measurements.

FIG. 4. The complex conductivity spectra determined from measurements acquired at an identical location on the graphene film inside nitrogen and ambient environment (~30-40% RH) where arrowheads indicate water vapour lines in a). By excluding water vapour line contributions, conductivity histograms are compared against nitrogen environment at different days in b) and c) at different relative humidities between 30-40% RH.