Graphene Conductance Uniformity Mapping

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ABSTRACT: We demonstrate a combination of micro four-point probe (M4PP) and non-contact terahertz time-domain spectroscopy (THz-TDS) measurements for centimeter scale quantitative mapping of the sheet conductance of large area chemical vapor deposited graphene films. Dual configuration M4PP measurements, demonstrated on graphene for the first time, provide valuable statistical insight into the influence of microscale defects on the conductance, while THz-TDS has potential as a fast, non-contact metrology method for mapping of the spatially averaged nanoscopic conductance on wafer-scale graphene with scan times of less than a minute for a 4-in. wafer. The combination of M4PP and THz-TDS conductance measurements, supported by micro Raman spectroscopy and optical imaging, reveals that the film is electrically continuous on the nanoscopic scale with microscopic defects likely originating from the transfer process, dominating the microscale conductance of the investigated graphene film.

KEYWORDS: Graphene, terahertz, micro four-point probe, metrology, imaging, electrical characterization, noninvasive characterization, spectroscopy

After the seminal work on graphene,1,2 its potential for use in lucrative applications has drawn much attention. Examples of electronic applications include integrated circuits,3 terahertz (THz) bandwidth RF electronics4 and spintronics,5 and photonic and optoelectronic applications include photovoltaic6 and light-emitting devices,7 saturable absorbers,8 optical limiters,9 nonlinear frequency conversion,10 and THz devices.11

In particular, extended areas of single- or few-layer graphene will have a strong, positive impact as transparent conductors in fields such as Hall bar devices or metal contact interfaces,27 and with a throughput that is orders of magnitude higher than alternative methods.

Methods are suitable for high throughput characterization or for investigation of the large-scale uniformity and quality of graphene films with respect to electronic properties.

In recent years, it has been shown that THz spectroscopy,18 used extensively to measure frequency-resolved conductance of bulk semiconductors19 and semiconductor nanostructures,20 is a powerful method for investigating the electronic response of graphene, either in the embodiment of THz Fourier-transform infrared spectroscopy21 or THz time-domain spectroscopy (THz-TDS),22–24 the latter also enabling ultrafast pump–probe investigations of THz conductance. It was also recently shown that the electronic response of single layer chemical vapor deposited (CVD) graphene can be imaged using THz-TDS.25,26 Because of the non-contact nature of the THz-TDS technique, mapping of unimpaired electronic properties, which can otherwise be affected by formation of ohmic graphene–metal contact interfaces,27–30 can be carried out without risk of damage and with a throughput that is orders of magnitude higher than alternative methods.

Received: April 25, 2012
Revised: August 31, 2012
Published: September 4, 2012
Similarly, micro four-point probes (M4PP),\textsuperscript{31} which were developed for the silicon industry\textsuperscript{32} to replace conventional macroscopic four-point probes, van der Pauw technique, and spreading resistance probes because these methods lack reliability\textsuperscript{33}−\textsuperscript{38} and spatial resolution\textsuperscript{32,39} when applied to advanced semiconductor layered structures, have recently been demonstrated as a tool for nondestructive characterization of graphene sheet conductance.\textsuperscript{40}

Here we demonstrate mapping of the electrical conductance uniformity by M4PP and non-contact THz-TDS as well as mapping of the Raman response of centimeter scale CVD graphene transferred onto silicon substrates covered with 90 nm SiO\textsubscript{2}, cf. Figure 1a, showing that THz-TDS and M4PP have potential for high-throughput metrology applications for large area graphene.

The measured conductance maps agree quantitatively with each other, showing a correlation indicative of the different length scales probed by the two techniques. Thus we unequivocally demonstrate that THz-TDS probes electrical conductance of graphene comparable to that measured in direct current (DC) transport measurements. The M4PP measurements probe the microscopic sheet conductance and are particularly sensitive to microscale electrical defects in the graphene sheet, while THz-TDS measurements probe the spatially averaged nanoscopic sheet conductance due to the very high frequency alternating current (AC) electric fields of the THz radiation. Through correlation of M4PP and THz-TDS maps, we find that microscopic defects, likely originating from the transfer process, dominate the microscale conductance of the investigated graphene film. Correlations with micro Raman spectroscopy (\(\mu\)-Raman) maps and optical images of the CVD graphene film support this notion.

All measurements were performed on large area CVD graphene thin films grown by copper catalyzed CVD technique on 25 \(\mu\)m thick copper foils using CH\textsubscript{4} as the carbon precursor. As our current implementation of the THz-TDS technique, based on transmission measurements, is not compatible with highly conducting and thus absorptive substrates, the graphene films were transferred onto high resistivity silicon wafers (\(\rho > 5.000 \Omega \text{ cm}\)). Two graphene samples grown by different recipes and transfer processes were investigated.

The first sample (labeled "sample 1" in the following) is the least apparent damaged graphene film with dimensions of 2 \(\times\) 2 cm. It was grown in a vertical furnace, where the copper foil was first annealed in hydrogen at a temperature of 1025 °C and pressure of 100 mTorr. The growth time was approximately 25 min during which the system was maintained at a pressure of 1500 mTorr and temperature of 1025 °C with a methane flow.

Figure 1. Combined THz-TDS, M4PP, Raman, and optical mapping of large area graphene on SiO\textsubscript{2}-on-Si substrate. (a) Sketch depicting the principle of parallel mapping of electrical conductance, Raman response and optical absorption on a single-layer large area graphene film by THz-TDS, M4PP, \(\mu\)-Raman, and optical microscopy; the combined information of these techniques facilitates determination of electrical uniformity on nanometer and micrometer length scales and correlation of electrical features to Raman and structural features. The sketch is based on actual data maps. (b) Illustration of the M4PP configuration switching technique used, where \(R_A\) and \(R_B\) are repeatedly measured and eight electrode combinations combine to obtain highly reproducible sheet conductance measurements via the dual configuration van der Pauw correction method. (c) Example of THz-TDS time-domain data showing multiple echoes from partial internal reflections in the SiO\textsubscript{2}-on-Si sample substrate. Sheet conductance extraction is based on the Fourier transform (FFT amplitude shown in inset) of the time-windowed 2nd transmitted pulse, \(E_2\), (indicated by gray shading) for areas with (black line) and without (red line) graphene on the surface of the wafer. (d) Schematic of fiber-coupled THz-TDS imaging experiment. The T-ray 4000 THz-TDS spectrometer uses fiber-coupled femtosecond near-infrared laser pulses and LT-InGaAs photoconductive antennas (PCA) to generate and coherently detect the time-dependent electric field of picosecond electromagnetic pulses. Multiple reflections in the sample substrate give rise to multiple echoes, \(E_{\text{out},1}, E_{\text{out},2}, \ldots, E_{\text{out},\infty}\). The sample is raster scanned in \(x-y\) plane for mapping.
of 2 standard cubic centimeters per minute (sccm) and a hydrogen flow of 0.5 sccm, similar to previously reported conditions for monolayer graphene growth.\textsuperscript{15,41} The grown graphene film was then transferred to a high resistivity silicon wafer by slow etching of the copper foil in a solution of 0.1 M ammonium persulfate (\((\text{NH}_4)_2\text{S}_2\text{O}_8\)) with a thin supporting polymethylmethacrylate (PMMA) layer. The PMMA was subsequently removed in acetone.

The second (labeled “sample 2”) is a \(6 \times 7\) mm graphene film with distinct optically visible damages. It was grown in a cold-wall CVD system using prediluted CH\(_4\) (5% in Ar) as carbon precursor. The deposition temperature was nominally 1000 °C and the growth time was 5 min. H\(_2\) and Ar were used as auxiliary gases, where the partial pressure of CH\(_4\) was kept very low (<0.01 mbar) to suppress the formation of multilayer graphene and enhance the quality and domain size of the graphene. More details about this CVD procedure are reported elsewhere.\textsuperscript{42--44} The as-deposited graphene was subsequently transferred onto high resistivity silicon by a standard wet transfer process using PMMA as mechanical support and a dilute, aqueous HNO\(_3\) solution to etch the copper film.\textsuperscript{15,42} Finally, the polymer was removed by acetone.

The Raman response of the samples was mapped using a Thermo Fisher Scientific DXR Raman microscope with a 532 nm excitation laser and a 2 \(\mu\)m spotsize. Spatial maps of the samples were produced with 200 and 75 \(\mu\)m lateral resolution for sample 1 and sample 2, respectively, providing spectroscopic information between 1100 and 3000 cm\(^{-1}\) (1 cm\(^{-1}\) resolution) in each pixel. The Raman maps are used as indicators of sample quality, which is in contrast to a direct correlation with our THz and M4PP maps. Thus the resolution of the Raman maps is chosen as a realistic compromise between image quality and total data acquisition time (10–12 h per mapping). Representative Raman spectra for the two CVD graphene samples, showing distinct D, G and 2D peaks, corresponding to single layer graphene, can be found in the Supporting Information.

M4PP mapping with up to 4000 individual measurements per sample was performed on a semiautomatic CAPRES MicroRsP-M150 scanner using a set current of 1 \(\mu\)A and lock-in technique (11 Hz). In contrast to previous work,\textsuperscript{40} the dual configuration van der Pauw method\textsuperscript{49} adapted to collinear four-point probes\textsuperscript{46} was used, providing far higher accuracy and lower variability. The two configurations labeled A and B are shown in Figure 1b along with examples of recorded data. For a simply connected infinite sheet, the dual configuration method completely eliminates in-line position errors and greatly reduces measurement errors on small regions with insulating boundaries in proximity of the four electrodes.\textsuperscript{57} The set current of 1 \(\mu\)A has been shown not to lead to sample damage, since it is significantly below the previously observed damage threshold of approximately 100 \(\mu\)A.\textsuperscript{48} The surface was detected using an integrated strain gauge cantilever sensor,\textsuperscript{48} and the cantilever electrodes were engaged to a nominal depth of 500 nm with a corresponding contact force of approximately 10 \(\mu\)N for each electrode. M4PP sheet conductance mapping was performed with an electrode pitch of 10 \(\mu\)m and a step size of 100 \(\mu\)m. To rule out potential time dependent sheet conductance variations, the measurement position chronology was randomized. Additional measurements, performed with electrode pitches ranging from 3 to 59 \(\mu\)m can be found in the Supporting Information.

THz sheet conductance maps were produced from THz-TDS data recorded using a Picometrix T-ray 4000 fiber-coupled spectrometer, cf. Figure 1c,d. The samples were raster scanned in 100 \(\mu\)m steps in the x–y direction of the focal plane between the fiber coupled emitter and detector units to form spatial maps. Partial internal reflections from the SiO\(_2\)–air interface in the substrate lead to a reflected signal that consists of multiple, periodic echoes with a temporal spacing given by the time-of-flight through the substrate, as illustrated schematically in Figure 1d. Through an analysis of the Fresnel coefficients for the sample geometry, where the graphene film is modeled as an infinitely thin conducting film, the complex sheet conductance, \(\tilde{\sigma}(\omega)\), is related to the complex transmission function, \(T(\omega) = \tilde{E}_{\text{out},2,C}(\omega)/\tilde{E}_{\text{out},2,S}(\omega)\), of the second transmitted pulses for areas with and without graphene coverage

\[
\tilde{\sigma}(\omega) = \frac{\pm n_A \sqrt{n_A^2 + 4 n_B n_S T(\omega) + 4 n_A^2 T(\omega)} - n_A^2 - 2 n_A n_B T(\omega)}{2 n_B Z_0 T(\omega)}
\]

where \(n_A = n_{\text{Si}} + 1, n_B = n_S - 1, n_S = 3.42\) is the refractive index of silicon and \(Z_0 = 377 \Omega\) is the vacuum impedance. Examples of \(\tilde{E}_{\text{out},2,C}(\omega)\) and \(\tilde{E}_{\text{out},2,S}(\omega)\) are shown in Figure 1c. We formed the average of 250 subsequent time-domain traces for the imaging, facilitating unambiguous determination of \(\tilde{\sigma}(\omega)\) with reliable spectroscopic information in the frequency range 0.1–1.5 THz\textsuperscript{49} for each pixel. See the Supporting Information for additional experimental details.

Figure 2 summarizes our measurements on sample 1. The optical image of sample 1 is shown in Figure 2a. Direct mapping of the magnitude and uniformity of \(\tilde{\sigma}(\omega)\) at 1.3–1.4 THz recorded by THz-TDS across the CVD graphene film with dimensions of approximately \(2 \times 2\) cm is shown in Figure 2b, revealing an electrically homogeneous film. The Raman maps of the graphene film are fairly homogeneous, as shown in Figure 2c,d with the exception of one region of spectral redshift of the Raman G peak, as shown in Figure 2e. This redshift,
which we also observe for the D and 2D peaks (see Supporting Information), is commonly interpreted as an indicator of local strain in the graphene film.\textsuperscript{51} This strain does not seem to have a significant influence on $\bar{\sigma}(\omega)$ of this particular graphene film, as the feature is not reproduced in the THz sheet conductance map in Figure 2b. Figure 3 shows examples of the extracted THz conductance spectrum measured in the central regions of the graphene film. \textsuperscript{51} The THz spot diameter is approximately 0.32 mm full-width-at-half-maximum (fwhm) in the 1.3–1.4 THz frequency range, inferred directly from in situ THz-TDS measurements. With increased bandwidth, the THz-TDS technique also allows determination of the Drude carrier scattering time through fitting of the characteristic Drude model to the spectrum.\textsuperscript{19,50} The measured THz spot diameter is approximately 0.32 mm full-width-at-half-maximum (fwhm) in the 1.3–1.4 THz frequency range, inferred directly from in situ measurement of the average rise distance on the left edge of the graphene film in Figure 2b (see Supporting Information for a plot of the spot diameter vs frequency). This results in some blurring, as variations on a smaller length scale are not accurately reproduced.

M4PP measurements carried out at 146 locations show a mean sheet conductance of $\sigma_{M4PP} = (0.64 \pm 0.13) \text{ mS}$. In comparison, THz-TDS measurements, extracted from the map shown in Figure 2b, show an average sheet conductance of $\sigma_{THz} = (0.768 \pm 0.077) \text{ mS}$ at 1.3–1.4 THz. With a measured relative standard deviation in repeatability of 3%, the large variation (20%) in $\bar{\sigma}(\omega)$ measured with M4PP as well as the discrepancy between $\sigma_{M4PP}$ and $\sigma_{THz}$ mean values might be explained by micrometer-scale defects and nonuniformity primarily affecting M4PP conductance. The measured sheet conductances (0.432 to 1.174 mS for THz; 0.248 to 0.973 mS for M4PP) correspond to between roughly 1.5 and 8 times the minimum DC conductance of graphene of $\sigma_{min} = 0.154 \text{ mS}$ found by Novoselov and co-workers,\textsuperscript{51} illustrating that both techniques reveal realistic graphene sheet conductances of comparable magnitude. While transport measurements\textsuperscript{51} tend to yield $\sigma_{min} = 4e^2/h = 0.154 \text{ mS}$ or higher,\textsuperscript{52} two-dimensional papers\textsuperscript{53} as well as optical spectroscopic investigations in the infrared\textsuperscript{54,55} and visible\textsuperscript{56} agree on a lower value of $\sigma_{min} = 4e^2/\hbar = 0.061 \text{ mS}$.

As an example of a measurement revealing significantly larger spatial variation, $\bar{\sigma}(\omega)$ was mapped across sample 2, a 6 × 7 mm CVD graphene film with distinct, optically visible inhomogeneities (see Figure 4a) by THz-TDS and M4PP techniques, cf. Figure 4b,c.

The THz and M4PP sheet conductance maps are in good qualitative agreement with the exception of a bright spot in the upper left corner of the THz image. This feature likely reflects a strongly scattering particle of high dielectric contrast, possibly a small grain of residual copper. Convolution of the M4PP data with a 2D Gaussian profile of fwhm = 0.32 mm, matching the THz spot size, accurately reproduces most features of the THz image (see Supporting Information).

A comparison of THz and M4PP maps with spatially resolved $\mu$-Raman measurements reveals a strong spatial correlation, most prominent between $\bar{\sigma}(\omega)$ and the Raman G and 2D peak heights, which follow each other closely (see Supporting Information).

Figure 3. Spectrally resolved sheet conductance of the two graphene films, measured by THz-TDS. Characteristic length scales are based on an estimated diffusion constant of $D = 66 \text{ cm}^2/\text{s}$. Triangles represent Re($\sigma$) and circles represent Im($\sigma$). The spectra are obtained in the center of Figure 2b (sample 1, blue points) and in the central conducting part of Figure 4b (sample 2, red points). The blue and red horizontal bands indicate the average real sheet conductances of the two samples. The gray horizontal band indicates the average imaginary sheet conductance (1.3–1.4 THz), (c) M4PP sheet conductance map, and (d) G peak height $\mu$-Raman map.
Figure 5. THz/M4PP correlation analysis. (a) Correlation diagram of THz and M4PP sheet conductance measurements for sample 1 (dark gray triangles) and sample 2 (light gray, blue, and red circles). The full black line indicates 1:1 correlation. (b) Sample map showing pixel positions of correlation data for sample 2. In (a) and (b), the data subset with $\Gamma = \sigma_{\text{M4PP}}/\sigma_{\text{THz}} > 1.1$ is plotted as red dots and the data subset with $\Gamma = \sigma_{\text{M4PP}}/\sigma_{\text{THz}} < 0.4$ is plotted as blue dots. The red dots tend to cluster near the edges of the sample, while the blue dots dominate areas with large holes and other distinct visible transfer damages. (c) Distribution of measured resistance ratio $R_\parallel/R_\perp$ in the dual configuration M4PP map shown in Figure 4 (turquoise bars), Monte Carlo simulation of $R_\parallel/R_\perp$ distribution for an infinite, continuous conducting sheet with 500 nm normal distributed electrode position errors (dashed, black line) and running average of the measured dual configuration sheet conductance as a function of $R_\parallel/R_\perp$ (full, orange curve).

Supporting Information). The Raman G peak height map reproduces many of the sheet conductance features, as shown in Figure 4d. Correlated variations in the G and 2D peak heights most likely reflect variations in the local graphene areal coverage, indicating that the THz-TDS and M4PP conductance of this graphene film is mainly influenced by the local density of rips and defects induced by the transfer or by incomplete growth coverage. Other parameters identifiable by $\mu$-Raman analysis, such as atomic defects, doping level and strain seem to be of secondary importance. There are also spatial features in the measured sheet conductance that are not reflected in the $\mu$-Raman data (see Supporting Information for additional Raman maps), showing that direct sheet conductance mapping of CVD graphene films provide valuable additional information about sheet conductance uniformity that cannot be inferred from Raman analysis.

A quantitative correlation analysis between THz and M4PP images of sample 2 (Figure 4b,c) is shown in Figure 5a,b, where the corresponding values for $\sigma_{\text{M4PP}}$ and $\sigma_{\text{THz}}$ have been plotted against each other for all pixels where the M4PP measurement yielded a finite and nonzero conductance. The subset of points with $\Gamma = \sigma_{\text{M4PP}}/\sigma_{\text{THz}} > 1.1$, shown with red dots in Figure 5a,b, is related to a lowering of the measured $\sigma_{\text{THz}}$ near edges of the film due to spot size blurring. If the measurements caused by this edge effect are ignored, it is evident that there is a tendency for the M4PP sheet conductance to be lower than that measured by THz-TDS. Although based on a smaller measurement population, the same tendency is observed in the correlation plot of THz and M4PP measurement from sample 1, shown in Figure 5a. As will be discussed below, this behavior stems from the different ways in which THz and M4PP measurements are affected by micrometer-scale defects such as rips, wrinkles (transfer defects) and domain boundaries (growth defects) in the graphene film.

The M4PP conductance measurement probes carrier transport on the scale of the 10 $\mu$m electrode pitch and is therefore very sensitive to microscopic defects. Riplike defects or domain boundaries smaller than the electrode pitch of 10 $\mu$m may substantially decrease the measured $\sigma_{\text{M4PP}}$ even by orders of magnitude, compared to the case of a defect-free sheet.$^{57,58}$ Also insulating rips or boundaries of dimensions similar to the electrode pitch can in the worst case result in an underestimation of the sheet conductance by up to a factor of 2.$^{47}$ The presence of a high density of defects of dimensions similar to the electrode pitch is indeed indicated in the graphene sample under investigation by the observed distribution of measured four-point probe resistance ratios, $R_\parallel/R_\perp$ (A and B configurations shown in inset of Figure 5c). For the case of a continuous conductive sheet (2D conductance), we find that a distribution of resistance ratios will result from variations in the absolute electrode positions with a peak centered at $R_\parallel/R_\perp = \ln 4/\ln 3 \approx 1.26$, cf. Monte Carlo simulations based on analytical calculation of the resistance ratio as function of Monte Carlo displacement of electrodes from their ideal positions.$^{59}$ In contrast to a continuous conductive sheet, the measured $R_\parallel/R_\perp$ distribution, shown in Figure 5c, displays features testifying that the graphene film cannot be assumed to be a simply connected conducting sheet on the scale of the electrode pitch. The narrow peak at $R_\parallel/R_\perp = 1.00$ is a distinctive trait of electrically conductive wirelike structures (1D conductance) or otherwise highly confined structures on the scale of the electrode pitch, whereas the broader distribution centered on approximately $R_\parallel/R_\perp = 1.15$ indicates a defected electrical discontinuous conductive film, containing multiple insulating boundaries of dimensions similar to the electrode pitch in proximity of the four electrodes, as also seen for small samples.$^{47}$ From the behavior of the orange curve in Figure 5c, calculated as the running average of the $\sigma_{\text{M4PP}}$ values, it is also apparent that the M4PP sheet conductance shows a distinct drop in magnitude for the measurements with $R_\parallel/R_\perp$ close to 1.00, indicating that this type of defect is associated with severely degraded microscale conductance. More specifically, measurements with variable electrode pitch (shown in Supporting Information) show that in a region with very low conductance, the $R_\parallel/R_\perp$ ratio approaches 1.00 and the conductance exhibits an increase for smaller electrode pitch (3 and 6 $\mu$m), while no significant dependence on electrode pitch appears in a region of high conductance, where the measured $R_\parallel/R_\perp$ ratio is also closer to the ideal 2D case. This is in good agreement with our interpretation that the M4PP sheet conductance is dominated by a high density of defects on the...
scale of the electrode pitch, and that this shows up as regions with laterally constricted or even wirelike conductance behavior.

Because of its AC nature, THz-TDS on the other hand probes carrier transport at a characteristic length scale given by the probing frequency and the material diffusion constant. Under the assumption of a diffusive transport regime, the characteristic length scale can be estimated as

\[ L = \sqrt{\frac{D}{2\pi f}} \]  

(2)

\[ D = \frac{E_\text{F} \sigma_s}{2n_e e^2} = \frac{E_\text{F} \mu}{2e} \]  

(3)

where \( L \) is the characteristic length scale, \( D \) is the diffusion constant, \( f \) is the frequency, \( E_\text{F} \) is the Fermi level, \( \sigma_s \) is the sheet conductance, and \( \mu \) is the carrier mobility. \( L \) is on the order of 10^{-8} to 10^{-7} m (approximately 100 and 30 nm at 0.1 and 1.5 THz, respectively, as indicated in Figure 3) for an estimated \( D = (66 \pm 15) \text{ cm}^2/\text{s} \) (corresponding to a Hall mobility \( \mu = (3.3 \pm 0.7) \times 10^5 \text{ cm}^2/(\text{Vs}) \) measured in a high-conductance area and thus an estimated Fermi level of \( E_\text{F} = (0.40 \pm 0.04) \text{ eV} \). This means that the measured THz conductance characterizes the spatially averaged nanoscopic conductance of the graphene film and is thus far less affected by the microscopic defects found to greatly affect the M4PP conductance of this graphene film. The THz conductance is, however, highly sensitive to defects on the nanoscopic scale. The THz conductance measured on sample 2 that displays no significant frequency dependence, cf. Figure 3, is evidence of an electrically homogeneous and continuous film on the scale from a few tens of nanometers to a few hundred nanometers. Careful edge-scan experiments (not shown here) have revealed that the observed drop in THz sheet conductance at the low end of the spectrum is caused by the low frequency parts of the THz spot extending outside the area with uniform graphene coverage, as indicated in the inset of Figure 3, and the small peak observed at 1.1 THz in Re(\( \sigma_s \)) is an artifact caused by the water absorption line of ambient air.

The behavior of the graphene film as a continuous sheet on the nanoscopic transport length scale of THz conductance measurements in contrast to its behavior as a highly deflected sheet on the macroscopic transport length scale of the M4PP conductance measurements is the most obvious explanation for the discrepancy between THz-TDS and M4PP sheet conductance measurements. These two results in combination suggest that this sample is electrically continuous on the few tens to a few hundred nanometer length scale while dominated in its nanoscale electrical response by a high density of insulating defects of dimensions similar to the M4PP electrode pitch of 10 \( \mu \text{m} \). The origin of such insulating nanoscale defects could be damage occurring during the transfer process as well as incomplete growth coverage or crystal growth defects, as certain graphene crystal domain boundaries have been shown to produce perfectly reflecting interfaces for low energy charge carriers. For sample 2, however, it is likely that the defects are transfer-related as the typical domain size obtained with the low partial pressure growth procedure is around 200 \( \mu \text{m} \). This conclusion is supported by the fact that the pixels shown as blue dots in Figure 5a,b with \( \Gamma = \sigma_{\text{M4PP}}/\sigma_{\text{THz}} < 0.4 \), that is, pixels where M4PP sheet conductance is most substantially lowered by microscale defects, tend to cluster around holes in the film and regions of very distinct optically visible transfer damage. \( \mu \)-Raman mapping results also support this notion, as they indicate strong correlation between M4PP and THz-TDS sheet conductance and graphene coverage.

Conclusions. In summary, we demonstrate direct, quantitative mapping of the sheet conductance of cm-scale CVD graphene films by M4PP and non-contact THz-TDS, facilitating characterization of the electrical uniformity of large area graphene films. We have shown that the THz-TDS measurement probes the spatially averaged nanoscopic transport properties of the graphene film while the M4PP microscopic transport measurement is highly sensitive to microscale defects. The THz conductance measurement thus provides the natural upper limit for M4PP sheet conductance measurement in graphene. A correlation analysis of quantitative M4PP and THz-TDS mappings of the sheet conductance of a large area CVD graphene film reveals that the film is electrically continuous on the characteristic length scale of a few tens of nanometers to a few hundred nanometers, associated with the THz-TDS measurement, while its microscale sheet conductance, probed by M4PP, is dominated by a high density of insulating defects with dimensions similar to the electrode pitch of 10 \( \mu \text{m} \). \( \mu \)-Raman mapping of the sample shows that both M4PP and THz-TDS conductances are strongly correlated to the graphene coverage, indicating that the microscopic insulating defects originate from the transfer process or from incomplete growth coverage.

Both M4PP and THz-TDS conductance mapping, as demonstrated and quantified here for cm-size graphene areas, are immediately scalable to full wafer dimensions and straightforwardly extended to work on a wide range of substrates, including thin, flexible polymers and doped semiconductors. A THz-TDS scan time of less than 1 min (1 ms/pixel) for a 4" wafer is technologically possible today (5 s/pixel for M4PP), making this technique particularly promising as a high-throughput, non-contact metrology tool for mapping of the spatially averaged nanoscopic conductance on wafer-scale graphene. In a wider perspective, the application of THz-TDS for nanoscopic conductance mapping can be extended to various electrically nonuniform or structured materials, such as for instance polymer-based, polycrystalline or structured photovoltaic materials. In addition, the combination of M4PP and THz-TDS offers the exciting potential of directly mapping both the Hall mobility and the carrier scattering time across wafer-scale areas of graphene films without need for postprocess patterning.

In emerging applications requiring up to square meter dimensions of graphene (electronics, displays, touch screens, photovoltaic applications), rapid, quantitative, contact-free inline characterization of the conductance is of vital importance. We believe that the results presented here will help pave the way toward that technologically important goal.

ASSOCIATED CONTENT

Supporting Information

Detailed descriptions of THz-TDS experimental method. Supporting Raman spectroscopy measurements, Raman imaging measurements, M4PP measurements with variable electrode pitch, and M4PP data analysis. This material is available free of charge via the Internet at http://pubs.acs.org.
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Notes
The authors declare no competing financial interests

ACKNOWLEDGMENTS

This work was financially supported by the Danish Council for Independent Research, Technology and Production Sciences (FTP), by the National Sciences and Engineering Council (NSERC) and by the Carlsberg Foundation. Center for Individual Nanoparticle Functionality (CINF) is sponsored by the Danish National Research Foundation. J.D.B., D.H.P., P.B., and P.U.J. conceived the experiments. J.D.B. performed all THz-TDS and μ-Raman experiments. D.H.P. performed all M4PP experiments with support from P.F.N., J.S., E.W., M.H., and A.Y. prepared the graphene samples. J.D.B. analyzed the THz-TDS data with support from P.U.J. and D.G.C. D.H.P. analyzed the M4PP data with support from O.H. M.H. analyzed the μ-Raman data. J.D.B., D.H.P., P.U.J., and P.B. carried out the correlation analysis of THz-TDS, M4PP and μ-Raman results with comments by D.G.C., M.H., and J.S. J.D.B. wrote the paper with comments by all authors.

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Supporting Information for

Graphene conductance uniformity mapping

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**THz-TDS experimental details**

THz sheet conductance maps were produced from THz-TDS data recorded using a Picometrix T-ray 4000 fiber-coupled spectrometer, cf. Figs. 1(b) and (c) in the main text. The spectrometer uses femtosecond near-infrared laser pulses and LT-InGaAs photoconductive antenna (PCA) chips to generate and coherently detect the electric field of ultra short THz electromagnetic pulses in the time domain$^1$. The samples were raster scanned in the x-y direction in the focal plane between the fiber coupled emitter and detector units to form spatial maps. Two polyethylene (PE) lenses were used to achieve better focusing and thus improved spatial resolution. Partial internal reflections from the SiO$_2$-air interface in the substrate lead to a reflected signal that consists of multiple, periodic echoes with a temporal spacing given by the time-of-flight through the substrate, as illustrated schematically in Fig. 1(c) in the main text. Time windowing and subsequent Fourier transformation gives access to the amplitude and phase of the frequency content of each of the echoes $E_{\text{out},1}(\omega), E_{\text{out},2}(\omega), …$ for every pixel in the map. The more reflections the THz pulse undergoes at the graphene-covered interface, the higher the accumulated graphene response will be. We apply an analysis which relies on the 2$^{nd}$ transmitted pulse in the transmitted pulse train, as shown in Fig. 1(c) in the main text, as we found this to be the optimum trade-off between graphene signal magnitude and noise level. The inset of Fig. 1(b) in the main text shows the frequency-dependent amplitude of the 2$^{nd}$ transmitted pulse $E_{\text{out},2}(\omega)$ recorded at a pixel covered by graphene (black traces) and without graphene (red traces). On the basis of an analysis of the Fresnel coefficients for the given sample geometry, where the graphene film is modeled as an infinitely thin conducting film with a complex sheet conductance $\sigma_s(\omega)$, transfer functions relating each of the consecutive echoes to the input field can be derived for areas with and without graphene coverage.
The graphene sheet conductance is then related to the ratio between measured transmitted fields from sample areas with and without graphene coverage by

\[
\frac{\tilde{E}_{\text{out},2,G}(\omega)}{\tilde{E}_{\text{out},2,\text{Si}}(\omega)} = \frac{(n_{\text{Si}}+1)^2 (n_{\text{Si}} - 1 - Z_0 \tilde{\sigma}_s(\omega))}{(n_{\text{Si}}-1)(n_{\text{Si}} + 1 + Z_0 \tilde{\sigma}_s(\omega))^2}
\]

(S.1)

Where \( n_{\text{Si}} = 3.42 \) is the refractive index of silicon and \( Z_0 = 377 \, \Omega \) is the vacuum impedance. The dielectric response of the 90-nm SiO\(_2\) layer is so small that it can safely be ignored in the analysis.

Inverting equation (S.1) results in an analytical expression for the complex frequency-dependent sheet conductance:

\[
\tilde{\sigma}_s(\omega) = \pm n_A \sqrt{n_i^2 + 4n_in_b \tilde{T}(\omega) + 4n^2_b \tilde{T}(\omega)} - n_i^2 - 2n_in_b^2 \tilde{T}(\omega)
\]

\[
= \frac{2n_b Z_0 \tilde{T}(\omega)}{2n_b Z_0 \tilde{T}(\omega)}
\]

(S.2)

, where \( \tilde{T}(\omega) = \frac{\tilde{E}_{\text{out},2,G}(\omega)}{\tilde{E}_{\text{out},2,\text{Si}}(\omega)} \), \( \tilde{E}_{\text{out},2,G}(\omega) \) is the complex Fourier transform of second transmitted pulse through a graphene-covered area, \( \tilde{E}_{\text{out},2,\text{Si}}(\omega) \) is the complex Fourier transform of the second transmitted pulse through an area without graphene, \( n_A = n_{\text{Si}} + 1 \), \( n_B = n_{\text{Si}} - 1 \), \( n_{\text{Si}} = 3.42 \) is the refractive index of silicon and \( Z_0=377 \, \Omega \) is the vacuum impedance. We formed the average of 250 subsequent time-domain traces for the imaging, resulting in data with reliable spectroscopic information in the frequency range 0.1-1.5 THz.

**THz-TDS mapping resolution**

The resolution of the THz-TDS sheet conductance mapping technique is evaluated from in-situ measurements on the THz-TDS sheet conductance mapping of ‘sample 1’. The average rise distance on the left edge of the THz sheet conductance image of ‘sample 1’ in Fig. 2(b) is evaluated as a function of frequency to produce plot of the spot size FWHM vs. frequency. The result is shown in supporting figure 1.
Supporting Figure 1: THz spot size FWHM vs frequency. The spot size is from the average rise distance on the left edge of the THz sheet conductance image of ‘sample 1’ in Fig. 2(b). This analysis reveals a spot size FWHM that is decreasing with increasing frequency, as is expected. The spot size in the 1.3-1.4 THz frequency range of interest is found to be approximately 0.32 mm FWHM.

Raman spectroscopy and imaging
Supporting Figure 2 shows Raman spectra for the two CVD graphene samples under investigation, showing distinct 2D, G and D peaks, are indicative of monolayer graphene containing few crystal defects.

Supporting Figure 2: Representative Raman spectra for CVD graphene films ‘sample 1’ and ‘sample 2’.

Supporting Figure 3 shows u-Raman maps of ‘sample 1’, showing the spectral positions of D, G and 2D peaks as well as the ratios of the G/d and 2D/G peaks. A region of spectral redshift is observed in all 3 positional maps, indicating local strain in the graphene film. The peak ratio maps are rather uniform and featureless.
Supporting figure 3: µ-Raman maps of D, G and 2D peak spectral positions and G/D, 2D/G peak ratios for ‘sample 1’

Supporting figure 4 shows µRaman maps of ‘sample 2’, showing height and spectral position and peak ratios of all 3 main peaks – 2D, G and D. Of all 6 maps, the G and 2D peak heights show the strongest correlation with the observed sheet conductance maps. The G and 2D peak height follow each other quite closely, indicating that graphene coverage is the main influence on these two parameters. This is also indicated in the maps of the peak height ratios G/D and 2D/G.
Supporting figure 4: µ-Raman maps for ‘sample 2’. From top to bottom the maps show peak height (top), peak spectral position (middle) and (bottom) peak height ratios G/D and 2D/G.

M4PP sheet conductance map blurring of ‘sample 2’

To more easily compare THz-TDS and M4PP sheet conductance maps, the spot size blurring of the THz-TDS conductance map of ‘sample 2’ can be compensated for by introducing a blurring of the M4PP sheet conductance map of ‘sample 2’. The M4PP sheet conductance map (supporting figure 5) is blurred with a Gaussian profile of 0.32 mm FWHM, which was found to be the resolution of the THz-TDS sheet conductance map. The resulting map shows a very high degree of resemblance with the THz-TDS (supporting figure 6) sheet conductance map of the same sample, except for the bright spot in the upper left corner of the THz-TDS conductance map.
Variable electrode pitch M4PP measurements

Examples of M4PP dual configuration sheet conductance data from a representative highly conducting region and a representative poorly conducting region is presented here. The data is obtained from 7 different A and B configurations of a 12 point probe, each with different electrode pitch. The 12 point probe was moved in 6 steps of 5 μm, measuring 7 dual configuration sheet conductances with different electrode pitches in each engage. Supporting figure 7 shows the mean sheet conductance as a function of probe pitch. Supporting figure 8 shows the full dataset of sheet conductance and \( R_A/R_B \) for individual engages and probe pitches in the two regions. The data shows that in a region of high conductance, where \( R_A/R_B \) is closer to the ideal 2D case of 1.26, the measured four point probe sheet conductance shows no significant dependence on electrode pitch. In contrast, the region with very poor conductance shows a \( R_A/R_B \) ratio that deviates strongly from 1.26 and is often measured to be close to 1.00, and a sheet conductance that increases with smaller electrode pitches.
Supporting figure 7: average M4PP dual configuration sheet conductance of 6 engages as a function of electrode pitch for a highly conducting region and a poorly conducting region on 'sample 2'.

Supporting figure 8: M4PP dual configuration sheet conductance and $R_A/R_B$ values for different electrode pitches and positions along two line-scans in a highly conducting region and a poorly conducting region on 'sample 2'. The data is recorded with a 12 point probe, facilitating 7 different equidistant M4PP configurations, in 6 engages with 5 µm spacing.
