Graphene conductivity mapping by terahertz time-domain reflection spectroscopy

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Abstract: We present a combination for centimetre scale quantitative graphene conductivity mapping by terahertz time-domain transmission and reflection spectroscopy in the frequency range 0.5 *THz* to 2.5 *THz*. The results agree well with each other and show that a higher signal-to-noise ratio is acquired through reflection measurement as a result of less influence of pollutants on the back of the substrate. Therefore, we can use terahertz reflection spectroscopy for graphene conductivity on any non-metallic substrates including substrates that THz wave cannot get through well. The graphene conductivity is well fitted by the Drude-Smith formula, which indicates the remarkable impact of carrier backscattering. Furthermore, we employ THz time-domain reflection spectroscopy for graphene conductivity mapping of a graphene/Si sample and find regional differences of the conductivity which can contribute to graphene surface plasmon polaritons and graphene modulators.

Keywords: Graphene conductivity, Terahertz spectroscopy, Transmission, Reflection, Drude-smith

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1. Introduction

Graphene with the form of a two-dimensional, atomic-scale, honey-comb lattice, has become a hot topic in plenty of applications such as terahertz sources [1-4], transparent electrodes [5], light-emitting devices [6], integrated circuits [7] and THz devices including modulators [8], detectors [9] and oscillators [10] since it was isolated and characterized in 2004 by Geim and Novoselov [11-16]. Recently, THz spectroscopy [17] has been shown great advantages for studying the electronic response of graphene [18-21] compared with scanning tunneling microscopy and atomic force microscopy measurements, which may be not available for the electrical characterization of large area graphene. However, most measurements on graphene conductivity are taken by terahertz time-domain transmission spectroscopy (TTDTS) while little is by terahertz time-domain reflection spectroscopy (TTDRS), but not all substrates allow THz wave to go through efficiently. In this work, TTDTS and TTDRS are adopted respectively for the conductivity mapping of a damaged large area chemical vapor deposited graphene film transferred onto a quartz substrate and TTDRS is used for the conductivity mapping of a single layer graphene film transferred onto a low resistivity Si substrate for which THz wave can hardly get through.

2. Experimental methods

2.1 Material preparation

A chemical vapor deposited graphene film with dimensions of about 1×1 *cm* was transferred onto a 3 *mm* thick quartz substrate of 1 *inch* in diameter. The graphene was damaged during the transfer and storage process. Another chemical vapor deposited graphene film with dimensions of about 1×1 *cm* transferred onto a low resistivity Si ($\rho < 0.01\ \Omega$.cm) substrate of approximately 0.5 *mm* in thickness is also prepared, for which THz wave cannot efficiently transmit.

2.2 Experiments

TTDTS and TTDRS were obtained by a TPS (THz Pulse Imaging and Spectroscopy) spectra 3000 assembled by the British company TeraView Ltd by means of a raster scanning on the graphene/quartz sample in 0.1 *mm* steps in the x-y direction of the focal plane between the fiber coupled emitter and detector units through transmission and reflection configurations separately. And then we get TTDRS of the graphene/Si sample. After that by means of Fourier transform of TTDTS and TTDRS we gain terahertz frequency-domain transmission spectroscopy (TFDTS) and terahertz frequency-domain reflection spectroscopy (TFDRS) of graphene/quartz sample as well as TFDRS of graphene/Si sample in the 0.5-to 2.5-*THz* frequency range, which is used for graphene conductivity calculation and mapping.

2.3 Computing methods

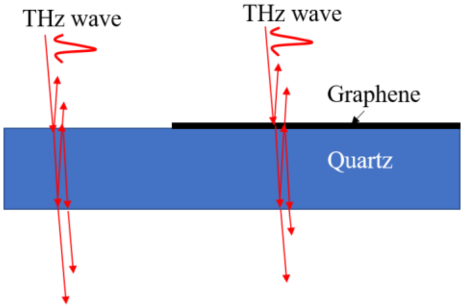

Fig. 1 THz pulses transmitted through the graphene-on quartz sample and the quartz substrate.

When a THz pulse enters into the graphene-on-quartz sample, a portion of the pulse is transmitted while the rest is reflected including multiple internal reflections at the front and back interfaces of the quartz substrate (Fig. 1). Also one of the measured transmitted and reflected time domain signals as well as frequency domain signals are shown in figure 2. The graphene was treated as an infinitely thin conducting film while the quartz as a lossless conducting medium. And the THz pulses are threaded vertically incident in both transmission and reflection measurements as incident angles are both very small. The 1th-order transmission coefficient through the air-graphene interface is given by Ref. [18]

$$t_g = \frac{2}{n+1+Z_0\sigma} \tag{1}$$

and the 1th-order transmission coefficient through the air-quartz interface is given by

$$t_0 = \frac{2}{n+1} \tag{2}$$

where n =1.96 is the refractive index of quartz, σ is the graphene conductivity, and $Z_0 = 377\ \Omega$ is the vacuum wave impedance. Combined with eqn. (1) and eqn. (2) we get the graphene conductivity given by

$$\sigma = \frac{\left(1/T_r - 1\right)\left(1+n\right)}{Z_0} \tag{3}$$

where $T_r = t_g / t_0$ is the relative transmission of the 1-th transmitted pulses for areas with and without graphene coverage.

While the 1th-order reflection coefficient through the air-graphene interface is given by

$$r_g = \frac{1-n-Z_0\sigma}{1+n+Z_0\sigma} \tag{4}$$

and the 1th-order reflection coefficient through the air-quartz interface is given by

$$r_0 = \frac{1-n}{1+n} \tag{5}$$

Combined with eqn. (4) and eqn. (5) we get the graphene conductivity given by

$$\sigma = \frac{\left(1-n\right)\left(1+n\right)\left(1-R_r\right)}{\left(\left(1-n\right)R_r + \left(1+n\right)\right)Z_0} \tag{6}$$

where $R_r = r_g / r_0$ is the relative reflection of the 1-th transmitted pulses for areas with and without graphene coverage.

For graphene/Si sample, we just need to use n = 3.42 for Si to substitute n =1.96 for quartz in equation (6) to get the conductivity. Using eqn. (3) and eqn. (6), we obtain the graphene conductivity mapping of graphene/quartz sample respectively via the transmission and reflection measurements as well as graphene/Si sample by the reflection measurement.

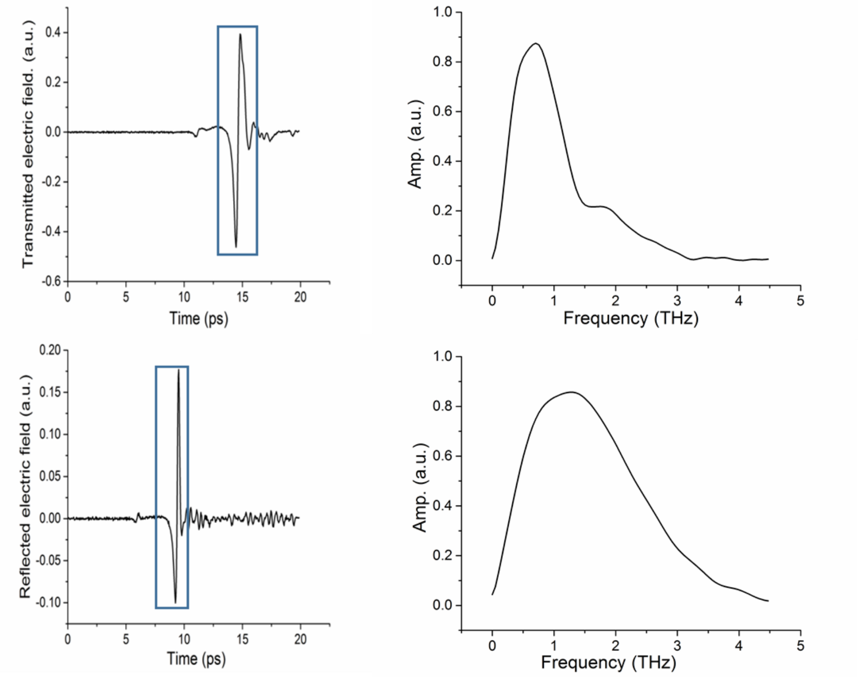

Fig. 2 Measured THz transmittance and reflectance signals in time domain and frequency. The marked rectangular areas are chosen one order transmitted and reflected signals for graphene conductivity computation.

3. Results and discussion

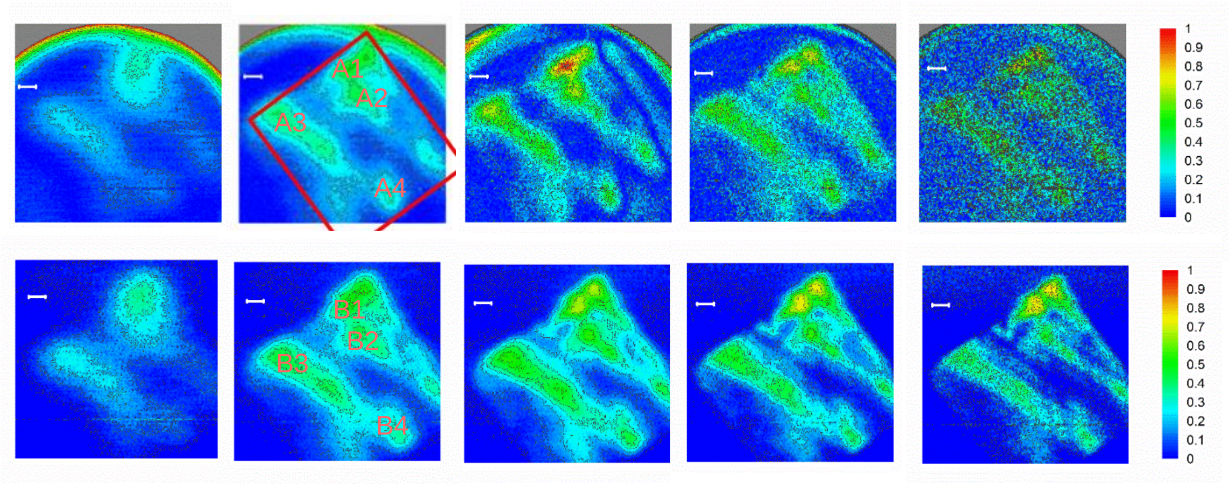

Fig. 3 THz conductivity mapping for graphene/quartz sample acquired from TTDTS (up) and TTDRS (down) respectively in the frequency range 0.5-2.5 *THz*, from left to right. Scale bars are 1mm.The area in the red rectangle is the rough position of graphene. Area labeled with acreage of about 1×1 mm^2 are chosen for results obtained by TTDTS and TTDRS comparison.

The graphene conductivity of graphene/quartz sample mapping obtained separately by TTDTS and TTDRS is shown in figure 3. We can easily find the discontinuous and inhomogeneous of graphene and the changing conductivity at different frequencies at first sight. Besides, it seems that higher signal to noise ratio is to get through TTDRS rather than that through TTDTS as a consequence of less influence of contamination on the back of the substrate. It also can be seen that transmitted signals introduce more background noise around 2 *THz* than reflected signals. Furthermore, the comparison of the graphene average conductivity achieved through TTDTS and TTDRS in chosen areas (size of about $1mm \times 1mm$ with center of labels in figure 2) in details and conductivity fitting according to Drude-Smith formula [20, 22] are shown in figure 4. The functional form of the Drude-Smith model depicts the complex conductivity of graphene as Ref. [20]

$$\sigma = \frac{W}{1-j\omega\tau}\left(1+\frac{c}{1-j\omega\tau}\right) \tag{7}$$

where W is a Drude weight, $\omega = 2\pi v$ is the frequency, τ is the carrier collision time, and c is a backscattering parameter, which is a measure of persistence of velocity. When $c = -1$, it accounts for full moment reversal of carriers, while $c = 0$ corresponds to the Drude model. Smith's model best represents our data when $c \approx -0.8$ to $c \approx -1$ for different parts of graphene region, as indicated by the best fit to our data shown in Figure 3.

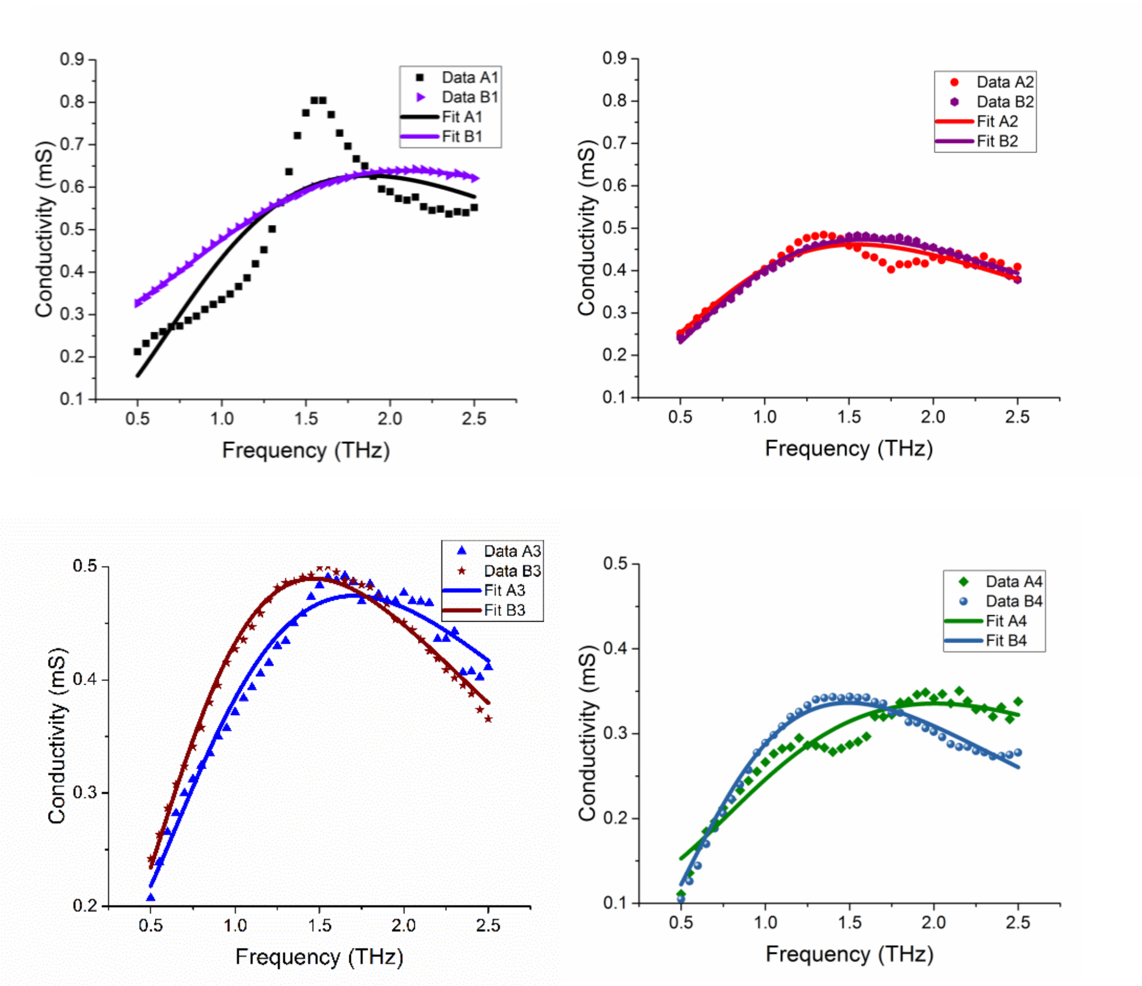

Fig. 4 Drude-Smith fit of the graphene average conductivity of chosen areas.

In figure 4 we can find that the graphene conductivity on quartz substrate achieved from TTDRS are better described by Drude-Smith formula, which may indicate less affect by pollutant on the back of substrate. Since the graphene conductivity is great fitted by Drude-Smith formula when $c \approx -0.8$ to $c \approx -1$, it accounts for the existence of prominent carrier backscattering. Moreover, despite that the positions labeled are not in strict one-to-one correspondence from TTDTS and TTDRS, the conductivity agrees well with each other, which declares that using TTDRS to get graphene conductivity is entirely feasible. So we employ TTDRS for the conductivity mapping of a graphene/Si sample and results at 0.8 *THz* is shown in Fig. 5.

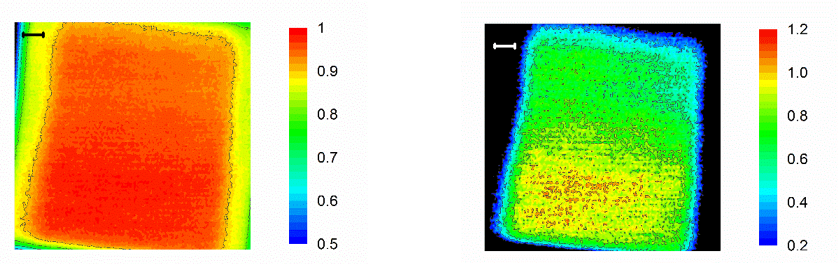

Fig.5 THz reflection pulse energy image (normalized, left) and the conductivity mapping (unit: mS, right) of graphene/Si sample at 0.8 *THz*. Scale bars are 1 *mm*. The red area like rectangle is approximately where graphene locates in.

As shown in Fig. 5, graphene on low resistivity Si is clearly visible with less damaged than the graphene on quartz sample. which demonstrates that TTDRS can be used to measure the conductivity of graphene on any nonmetal substrate with high signal to noise ratio. It is also displayed that the conductivity of the upper part of graphene is lower than the underpart, allowing manipulating and clipping graphene surface plasmon polaritons [23, 24], which can make contribution to numerous photonic functions and metamaterial concepts. Our results are well consistent with the related results of graphene conductivity grown on commercial Cu foils in Ref. [20].

4. Conclusions

In conclusion, we have obtained and compared the graphene conductivity by using terahertz time-domain transmission and reflection spectroscopy. Also we have adopted Drude-Smith formula to fit the conductivity range 0.5 *THz* to 2.5 *THz*. The well agreed results show that we can use TTDRS to acquire the graphene conductivity on any nonmetal substrate with high signal to noise ratio including some substrates that THz wave cannot get through efficiently. Furthermore, we have employed TTDRS to measure the graphene conductivity on a low resistivity Si substrate for which THz wave can hardly transmit and we have found that the different conductivity between the upper and the underpart graphene permitting for controlling graphene surface plasmon polaritons selectively. Our work may contribute to the intense research on the electrical and optical properties of graphene as well as a plenty of functional devices in the

THz range.

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