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Non-contact method for measurement of the microwave conductivity of graphene

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We report a non-contact method for conductivity and sheet resistance measurements of monolayer and few layers graphene samples using a high Q microwave dielectric resonator perturbation technique, with the aim of fast and accurate measurement. The dynamic range of the microwave conductivity measurements makes this technique sensitive to a range of imperfections and impurities and can provide rapid non-contacting characterisation. As a demonstration of the power of the technique, we present results for graphene samples grown by three different methods with widely differing sheet resistance values. [http://dx.doi.org/10.1063/1.4821268]

The remarkable properties of single- and few-layer graphene thin films have led to an explosion of activity.¹ ³ A number of different methods for preparing graphene thin films have appeared, and a wide range of experiments are being carried out on them.⁵ ¹² There is a great deal of variability in the number of different methods for preparing graphene thin films has been used previously to examine a variety of other materials.¹³,¹⁴ However, the advantage of our method is that exact permittivities of 11.6 (a-axis) and 9.4 (b-c plane) with a loss tangent of <10⁻⁵. It is usually used as a TE₀₁₁ micro-wave resonator with the electric field in the b-c plane. A plain low loss dielectric substrate, of thickness t₀, can be brought to a fixed position in relation to this sapphire puck resonator (see Figure 1(b)), and the resulting shift in both the resonant frequency Δf₀ and the linewidth Δw₀ can be measured, provided the quality factor of the sapphire resonator is high enough compared with the losses contributed by the substrate. Now take another, nominally identical substrate coated with a uniform layer of graphene of thickness tₐ (see Figure 1(c)). Place it in the same position relative to the sapphire puck and support quartz tubes in the copper housing (see Figure 1(d)).

Since tₐ ≪ t₀ and also tₐ ≪ δ₀, the electromagnetic skin depth of graphene at microwave frequencies, we may assume, to a good approximation, that the field distributions in the bare substrate and graphene coated substrate situations are the same. Thus, we may apply perturbation theory to evaluate the surface impedance of the graphene, provided that the complex permittivity and thickness of the bare substrate are known

\[ \Delta f_x = f_0 \left( \frac{(\varepsilon_x - 1)}{W} \int E^2 dV \right), \]  

(1)

where E is the field within the substrate and the integral is over the substrate volume. W is the total stored energy in the puck and substrate system. \( \varepsilon_x \) is real part of the substrate permittivity. As the assumptions above that the graphene layer is very thin, its presence in the second measurement will not significantly perturb the total field distribution in the system. However, the complex permittivity of the thin film may contribute significantly to the frequency shift and the linewidth shift

\[ \Delta f_x = f_0 \left( \frac{(\varepsilon_x - 1)}{W} \int E^2 dV + (\varepsilon'_x - 1) \int E^2 dV \right), \]  

(2)
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The aim of this measurement is to derive a surface resistance density. We know that the readily measurable quantities are \( \Delta f_s \) and \( \Delta w_s \), and \( \Delta f_t \) and \( \Delta w_t \) and the latter may be expressed as

\[
\Delta w_s = \int \left[ \varepsilon'' \frac{E^2 dV}{W} \right] df_s.
\]

Here, we have assumed that both for graphene and bare substrate, the electric field is uniform throughout the thickness; a reasonable assumption provided the substrate is much thinner than the height of the puck. This is confirmed by both finite element calculations and reversing the graphene sample so that the graphene is on the substrate surface further from the puck. The deduced conductivity of the graphene is the same (within \( \pm 10\% \)) for both orientations. The aim of this measurement is to derive a surface resistance (or sheet resistance) \( R_s \) value for the graphene film since this will also enable us to estimate the graphene conductivity (and the mobility if we are able to estimate the carrier density). We know that

\[
R_s = \frac{1}{\sigma_t}. \tag{6}
\]

There is a simple relationship between conductivity \( \sigma \) and imaginary component of the dielectric constant \( \varepsilon'' \)

\[
\sigma = 2\pi f_s \varepsilon_0 \varepsilon'' = \frac{2\pi f_s \varepsilon_0 (\Delta w_s - \Delta w_t) (\varepsilon'' - 1) t_s}{\Delta f_t t_s}. \tag{7}
\]

So finally, our expression for \( R_s \) becomes independent of graphene thickness \( t_s \)

\[
R_s = \frac{\Delta f_s}{2\pi f_s \varepsilon_0 (\Delta w_s - \Delta w_t) (\varepsilon'' - 1) t_s}. \tag{8}
\]

The TE\(_{011}\) resonance in the sapphire dielectric puck occurs at around 10.6 GHz. The presence of a 10 × 10 mm bare quartz substrate, placed directly on top of the sapphire resonator, shifts the frequency (downwards) in the range 50–200 MHz, depending on the spacing between them. This produces no significant reduction in the quality factor \( Q \) of the resonance, which at room temperature is around 1 × 10\(^4\). The presence of a single layer of graphene on such a quartz substrate produces a large reduction in \( Q \) value and a further small shift in the resonant frequency. In Figure 2, the upper trace shows an example of a resonance with plain quartz substrate and the lower trace shows a similar trace with a sample of CVD grown graphene\(^{12}\) transferred onto a nominally identical quartz substrate. Note the reduction \( Q \) by a factor of approximately 10 in the latter case.

The resonant frequency and linewidth are measured in transmission with a vector network analyser (VNA) being used to measure \( S_{12} \) as a function of frequency. The internal software of the VNA (HP 8720) is used to collect the centre frequency and 3 dB linewidth, but in addition, the full trace data (200 frequency points) are downloaded to a computer and a non-linear least squares fit routine is used to fit the data to a skewed Lorentzian lineshape by this method, we have found that the uncertainty in centre frequency and in

![FIG. 2. Measured S\(_{12}\) transmission versus frequency for both a bare quartz substrate (upper trace) and a quartz substrate with transferred CVD graphene (lower trace). The narrower resonance (higher Q) corresponds to the bare quartz sample and note that the linewidth is approximately 3 times greater for the CVD sample compared with bare quartz. Crosses are experimental points and solid lines are the Lorentzian fit to the data (NB: the two are almost indistinguishable to the eye).](image-url)
linewidth is reduced by a factor of 10, compared with the results output directly from the VNA.

For graphene samples with rather high conductivity, it has sometimes been necessary to reduce the influence of the graphene layer on the quality factor of the system by inserting a small quartz tube spacer a few mm in height, between the sapphire puck and the graphene coated and bare substrates (as shown schematically in Figure 1). In this way, the influence on the resonant properties is reduced so that the $Q$ value can be accurately measured.

In order to demonstrate the utility of the above dielectric resonator technique, we have made measurements on a number of samples of graphene grown by different techniques, possessing very different transport properties. In Table I, we compare liquid-phase grown graphene oxide (GO), subsequently reduced (rGO), CVD graphene grown on a copper catalyst layer, and then transferred to a clean quartz substrate (relative permittivity 4.4, 10 × 10 mm, and 0.5 mm thick). Finally, two separate samples of epitaxially grown graphene on SiC (relative permittivity 9.66, 5 × 5 mm, and 0.5 mm thick) are also shown. Note that the range of sheet resistance values measured spans almost four orders of magnitude, demonstrating the great sensitivity and dynamic range of the method. In our method, we can derive sheet resistance $R_s$ without the need to measure the thickness of the graphene since sheet resistance derived by Eq. (8) is independent of thickness.

It is clear from the results in Table I that, as would be expected, the rGO sample has a conductivity considerably higher than the as-grown GO sample for same thickness. It is the reduction process which converts the sample into a semimetallic state. Comparing the rGO and CVD sample conductivities, it is clear that the latter is more metallic than the former, again unsurprising given the nature of the wafer-scale growth process for CVD. For monolayer graphene on SiC, the conductivity is two orders of magnitude greater than the monolayer CVD graphene and the sheet resistance is nearly three orders of magnitude lower than the CVD sample.

The analysis presented above, and the results shown in Table I, confirms that the dielectric resonator technique provides a quick and straightforward method for analysing the conducting properties of graphene samples. Note that no patterning or electrical contacts are required, which may damage or compromise the sample quality. The sample can be placed on top of the puck or quartz spacer without requiring adhesive, another potentially damaging addition. The method has great sensitivity and dynamic range. We may estimate the expected uncertainty in the measurements made with this method. First, it is clear that the dimensions of the plain substrate and the graphene coated substrate should be as similar as possible. Any difference in dimensions will feed directly into the calculation of conductivity and sheet resistance through Eq. (8). Note that a 1% change in substrate thickness will produce a 1% change in calculated transport quantity. Equally, if graphene covers only X% of the substrate (X < 100%), the deduced graphene conductivity will be only X% of the full coverage value. Obviously some method is required to determine the coverage if possible but note that, if not, the measurement will pessimistically estimate the conductivity of the graphene, a satisfactory result from the point of view of quality control. A second indication of the expected uncertainty comes from a comparison of samples taken from equivalent regions on a larger wafer. These show conductivity and sheet resistance values which are usually within 10% of each other, suggesting that this is on the order of the upper limit on uncertainty to be expected. In addition, the reproducibility of samples with respect to a sequence of positional adjustments shows that this uncertainty is at most a few percent. Importantly, complex electromagnetic mode modelling is not required for this method, thus it shows great promise for rapid quality control and characterisation. It may be extended in future to cryogenic or elevated temperature measurement. We are also investigating the possibility that, based on using higher order puck resonator modes, it may prove to deduce the graphene mobility in a contact-free way, as well as sheet resistance and conductivity.

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### Table I. Summary of properties of monolayer CVD graphene, reduced graphene oxide on quartz substrates, and monolayer graphene on SiC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Graphene thickness (nm)</th>
<th>$f_0$ (GHz)</th>
<th>$\Delta f$ (MHz)</th>
<th>$\Delta \omega_c - \Delta \omega_t$ (MHz)</th>
<th>Conductivity $\sigma$ (S/m)</th>
<th>Sheet resistance $R_s$ ((\Omega/\square))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-layer reduced GO</td>
<td>0.4</td>
<td>10.5504</td>
<td>1.169</td>
<td>0.0243</td>
<td>$4.82 \times 10^7$</td>
<td>$48222$</td>
</tr>
<tr>
<td>1-layer CVD</td>
<td>0.4</td>
<td>10.4596</td>
<td>140.7</td>
<td>10.91</td>
<td>$1.92 \times 10^6$</td>
<td>$13038$</td>
</tr>
<tr>
<td>1-layer on SiC (sample 1)</td>
<td>0.4</td>
<td>10.5619</td>
<td>7.463</td>
<td>47.30</td>
<td>$2.03 \times 10^7$</td>
<td>$61.7$</td>
</tr>
<tr>
<td>1-layer on SiC (sample 2)</td>
<td>0.4</td>
<td>10.5600</td>
<td>5.057</td>
<td>73.38</td>
<td>$4.64 \times 10^7$</td>
<td>$26.97$</td>
</tr>
</tbody>
</table>