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Observation of multilayer graphene sheets using terahertz phase contrast microscopy

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Abstract. Although it is important for the study of graphene, identifying and characterizing the number of graphene layers is challenging. In this paper, we calculate graphene's transmission. The result shows that the phase change is more sensitive than the intensity change when light passes through graphene in some THz frequencies. Based on this fact, a simple route is presented for identifying the single or few layers of graphene sheets by using terahertz phase contrast microscopy (TPCM). The route is fast, and easy to be carried out.

Keywords. Graphene; terahertz radiation; surface conductivity; phase contrast microscopy; transmission function.

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1. Introduction

Graphene is an ideal two-dimensional material with unique optical [1], electrical [2], and mechanical properties [3] as well as anomalous quantum Hall effect [4–6]. It has recently attracted tremendous interest in both fundamental research and device application [7–13].

The physical, chemical and mechanical properties of graphene are strongly related to the number of layers. Scanning probe microscopy, such as atomic force microscopy (AFM), could identify graphene layers, but the scan area is restricted and the throughput is extremely low. Basically, scanning electron microscope (SEM) and transmission electron microscopy (TEM) can also, in principle, be used for identifying single or few layers of graphene sheets. However, the imaging typically induces a layer of contaminant in the exposed region [14]. Though Raman microscopy has proved itself a powerful tool for distinguishing graphene monolayers [15], the difference between two-layer and multilayer graphene sheets is not obvious and unambiguous in Raman spectra. Another possible way is to use 'naked eye' with common optical microscope. It is widely used to determine the thicknesses of thin films. However, this is not a quantitative method because of variation of the contrast from one laboratory to another [2]. For these reasons, an easy, fast and quantitative way to identify the number of graphene layers is needed.

In this paper, we calculate the transmission based on the boundary conditions and graphene's surface conductivity in the THz range. The phase change is more sensitive than the intensity change when light passes through graphene in some THz bands. So we propose a new optical device, terahertz phase contrast microscope (TPCM), for identifying and characterizing the number of layers in graphene sheets. Then the paper explains the principle of the TPCM. Simple measurement process and the expression of the number of layers N of unknown multilayer graphene sheets are finally given.

2. Transmission of graphene in the THz region

We consider that the graphene is illuminated by a plane wave (figure 1). The electric field of the incident light, reflected light and transmitted light are $\hat{x}E_x^{\mathrm{i}}$, $-\hat{x}E_x^{\mathrm{r}}$ and $\hat{x}E_x^{\mathrm{t}}$, respectively. The magnetic field of the incident light, reflected light and transmitted light are $\hat{z}H_z^{\mathrm{i}}$, $\hat{z}H_z^{\mathrm{r}}$ and $\hat{z}H_z^{\mathrm{t}}$ respectively. The boundary conditions are

$$\mathbf{n} \times [\mathbf{E}_2 - \mathbf{E}_1] = 0, \tag{1}$$

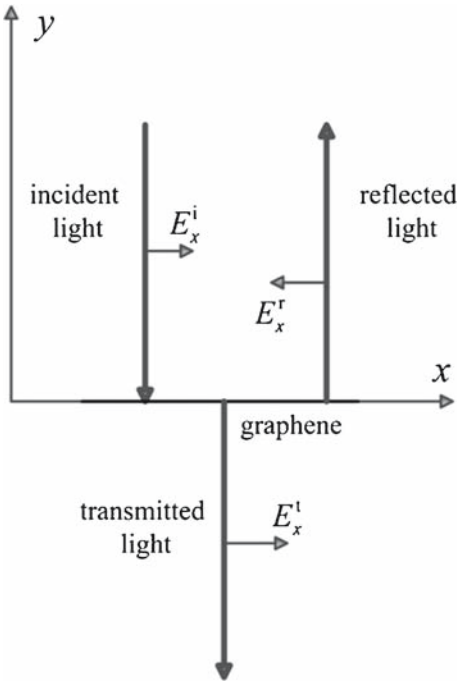

Figure 1. Interaction of an incident wave and graphene.

$$\mathbf{n} \times [\mathbf{H}_2 - \mathbf{H}_1] = \mathbf{J}_s. \tag{2}$$

E is the electric field and **H** is the magnetic field. The direction of the normal vector **n** is according to the reverse direction of the y-axis. Using the boundary conditions, we can get

$$H_z^i + H_z^r - H_z^t = J_s, \tag{3}$$

$$E_x^i - E_x^r = E_x^t. \tag{4}$$

We know

$$E_x^t/H_z^t = \eta, \quad E_x^r/H_z^r = \eta, \quad E_x^i/H_z^i = \eta, \tag{5}$$

$$J_s = \sigma_g E_x^t, \tag{6}$$

$$F = H_z^t/H_z^i. \tag{7}$$

From (3)–(7), transmission function can be evaluated as

$$F = \frac{1}{1 + \sigma_g \eta/2}, \tag{8}$$

where J_s is the electric surface current, η is the air wave impedance, σ_g is the surface conductivity of graphene and F is the transmission function of graphene.

In the THz range, the surface conductivity of graphene is a complex number with $\sigma_g = \sigma_r + i\sigma_i$ (the subscripts r and i stand for reflected and incident) and it depends on the angular frequency ω, temperature T and the chemical potential μ_c. Surface conductivity of graphene used in our simulations is derived within the random-phase approximation [16]

$$\sigma_g = \frac{2e^2}{\pi\hbar}\frac{k_B T}{\hbar}\ln\left[2\cosh\left(\frac{\mu_c}{2k_B T}\right)\right]\frac{\mathrm{i}}{\omega + \mathrm{i}\tau^{-1}} + \frac{e^2}{4\hbar}\left[\frac{1}{2} + \frac{1}{\pi}\arctan\left(\frac{\hbar\omega - 2\mu_c}{2k_B T}\right) - \frac{\mathrm{i}}{2\pi}\ln\frac{(\hbar\omega + 2\mu_c)^2}{(\hbar\omega - 2\mu_c)^2 + 4(k_B T)^2}\right], \tag{9}$$

where τ is the relaxation time, μ_c is the chemical potential, T is the temperature, e is the electron charge, $\hbar$ is the reduced Planck's constant, k_B is the Boltzmann's constant and $\omega = 2\pi f$ (f is radian frequency) is the angular frequency.

The term $\sigma_g\eta/2$ in expression (8) is defined as the complex A. So

$$A = \eta(\sigma_r + \mathrm{i}\sigma_i)/2. \tag{10}$$

σ_r and σ_i can be calculated using (9). The parameters $\tau = 1 \times 10^{-12}$ [17,18], $T = 300$ K and $\mu_c = 0$ eV. Figures 2 and 3 respectively present A and the ratio of its imaginary part and real part for different frequencies. So we get the complex number A and Im[A]/Re[A] for three different frequency points (table 1) (Im[A] is the imaginary part of A and Re[A] is the real part of A). The values for Im[A]/Re[A] are respectively 6.15 and 5.37 when the frequency points are 2 and 3. Hence the phase change is more sensitive than the intensity change when the frequency f is 2–3 THz.

In the region (2–3 THz), the number A is much less than 1 (table 1). Based on the Maclaurin formula of the

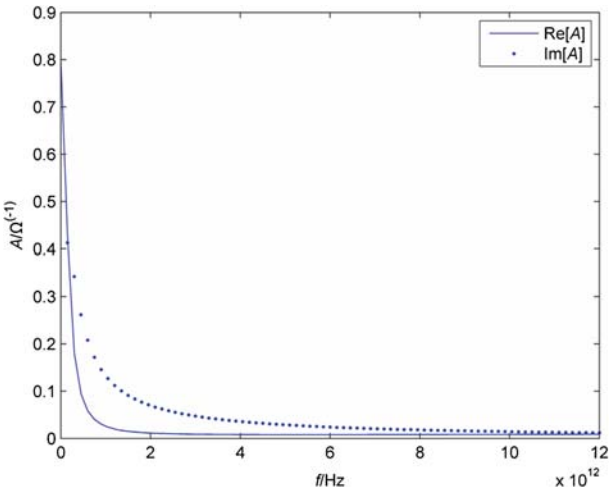

Figure 2. The number A for different frequencies.

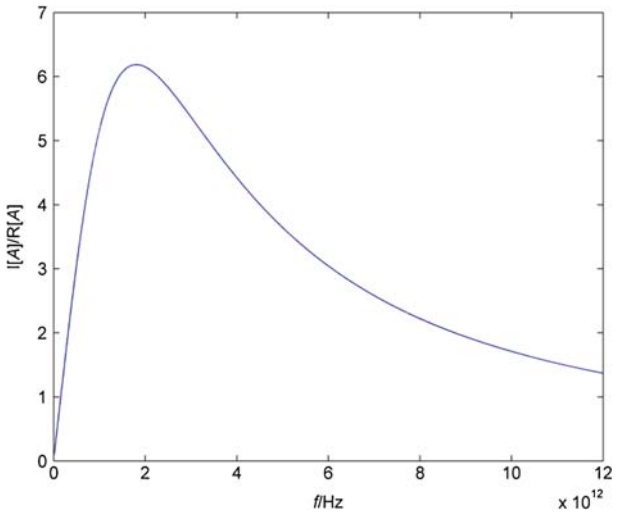

Figure 3. Ratio of the imaginary part and the real part of A for different frequencies.

function $y = 1/(1-x)$ and $y = \exp(x)$, eq. (8) can be estimated as

$$F = \exp(-\sigma_g \eta/2). \tag{11}$$

So we obtain

$$F = \exp[-\eta(\sigma_r + i\sigma_i)/2]. \tag{12}$$

When $\phi = -\eta\sigma_i/2$ (ϕ is a real function), we arrive at the following estimate from (12) (we neglect σ_r as σ_r is smaller than σ_i, for example, σ_i is 6.15 times larger than σ_r when f is 2 THz):

$$F = \exp(i\phi). \tag{13}$$

The expression (13) is the transmission function of a single graphene sheet. To two layers or multilayers, we define layer coefficient $t(x, y) = 2, 3, \ldots$, which shows that the number of layers are $t(x, y)$ for different points (x, y) of the object plane. The coefficient is discrete. So

$$\varphi'(x, y) = -\eta\sigma_i t(x, y)/2. \tag{14}$$

So (13) can be rewritten as

$$F'(x, y) = \exp[i\phi'(x, y)]. \tag{15}$$

Then a thin phase plate is placed in the back focal plane of the objective. The phase difference introduced by the plate represents a retardation or advance by a quarter of a period. Phase changes introduced by the object can be transformed into changes in intensity [19]

$$I(x', y') = |C|^2 [a^2 \pm 2a\phi'(x, y)], \tag{16}$$

where C is a constant. The coordinate (x', y') represents point of the image plane, corresponding to the point (x, y) of the object plane. For a plate that only retards or advances phase of the light which is incident upon it, $a = 1$; for a plate that also absorbs light, $a < 1$.

When the phase plate does not absorb any of the incident light ($a = 1$), eq. (16) can be written as

$$I(x', y') = 1 \pm 2\phi'(x, y). \tag{17}$$

The expressions (16) and (17) show that phase changes introduced by graphene sheets are transformed into changes in intensity, the intensity at any point of the image plane being directly proportional to the phase change due to the corresponding element of the graphene sheets.

3. Terahertz phase contrast microscope

Phase contrast imaging was first presented by Frits Zernike in the 1930s [20,21], and has been widely applied to biology for imaging transparent specimens since then. The paper introduces a new device – the TPCM. In the microscope, incident light is a monochromatic terahertz wave emitted by terahertz source such as quantum cascade lasers (QCLs). In figure 4, a two-Fresnel-lens (named lens 1 and lens 2) imaging system is used. The two lenses are terahertz lenses [22], which can be made of low-loss polymers [23,24], metamaterial [25], powders [26] and liquid [27]. The lenses can focus THz wave. Phase plate is at the centre focal plane of the two-lens system, and the object is at the back focal plane of the first lens (the Fourier plane). There is spatial separation in this plane between the undeflected beam and the diffracted light [28] when incident light passes through the object (graphene). The undeflected beam is focussed at the centre of the lens and the phase plate, but the diffracted light is spread throughout the plane (see figure 4). The phase plate makes use of the spatial separation by causing a $\pi/2$ relative phase

Table 1. The number A and Im[A]/Re[A] for different frequency points.

Frequency (THz)	2	2.5	3
A	0.0696i + 0 .0113	0.0563i + 0.0097	0.0474i + 0.0088
Im[A]/Re[A]	6.15	5.83	5.37

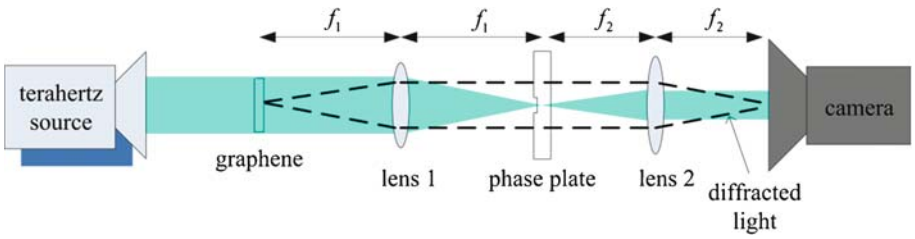

Figure 4. Schematic diagram of the terahertz phase contrast microscope.

shift between the undeflected beam and the diffracted light. The two beams are focussed on the image plane of the second lens where they form interference pattern. The pattern could be detected by the CCD camera. The technique converts phase shifts of terahertz wave passing through graphene to amplitude variations.

So the parameters can be set as follows: $f = 2$ THz, $\mu_c = 0$ eV and $T = 300$ K. Measurement process can be mainly as follows. First of all, a single graphene is taken as a reference, which has been identified by other methods. The intensity data I_1 is obtained using TPCM (figure 4). Next, the intensity information $I_N(x', y')$ of the unknown multilayer graphene sheets is also measured using TPCM. Finally, the number $N = [I_N(x', y') - 1]/(I_1 - 1)$ of layers of unknown multilayer graphene sheets can be calculated based on the intensity data of single-layer and multilayer graphene.

As seen above, first the intensity data of the monolayer graphene as a reference can be stored in the database. Secondly, once the intensity data of unknown multilayer graphene sheets are obtained using TPCM, the number of layers can be quickly calculated. So the method is quantitative, easy and fast, and not influenced by external conditions. It can be widely applied to identify graphene layers. This paper provides a way to detect 2D materials using optical microscopy. We can use TPCM to detect 2D materials when the phase change is more sensitive than the intensity change, whereas utilizing non-TPCM to detect 2D materials.

4. Conclusion

In this paper, we have calculated the transmission of graphene according to the boundary conditions and surface conductivity of graphene in the THz range. We note that the phase change is more sensitive than the intensity change when light passes through graphene in some Hz bands. Based on this fact, a new device, TPCM, has been proposed. Then we introduce the principle of the TPCM. We also show the measurement process and the expression of the number of layers N of graphene sheets. The results show that the TPCM can also be used to detect other 2D materials. The method is easy, fast and quantitative and so can be used in future research and application of 2D materials using graphene.

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