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Extracting the complex optical conductivity of mono- and bilayer graphene by ellipsometry

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A method for analysis of spectroscopic ellipsometry data is demonstrated to extract the optical conductivity of mono- and bilayer chemical-vapor-deposited graphene. We model graphene as a truly two-dimensional (2D) material with a sheet conductivity, rather than a phenomenological effective refractive index as has been used in the literature. This technique measures both the real and imaginary part of the optical conductivity, which is important for graphene optoelectronics and metamaterials. Using this method, we obtain broadband measurements of the complex optical conductivity for mono- and bilayer graphene from ultraviolet to mid-infrared wavelengths. We also study how chemical doping with nitric acid modifies the complex optical conductivity.

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Since the isolation of single-layer graphene in 2004, many other crystalline materials such as BN and MoS₂ have also been fabricated into atomically thin layers.^{1–3} They are now classified as two-dimensional (2D) materials, which have very distinct properties from their bulk counterparts; in principle, this reduced dimensionality requires a different description of the important physical quantities. For example, in a truly 2D material, the refractive index is not well-defined, since there is no rigorous definition for the induced polarization per unit volume. A better physical quantity to describe the optical properties of a truly 2D material is its optical conductivity, which is associated with the surface current generated by light.^{4–6} By comparing accurate measurements of the optical conductivity with theoretical predictions, one can gain knowledge of the underlying physics of the 2D material. Furthermore, 2D materials have become unique building blocks for more complicated and sophisticated structures, which create optical functionalities in photodetectors and metamaterials.^{7–10} Developing a simple and robust technique to measure the 2D optical conductivity has become crucial for further advance of using 2D materials in optoelectronic and metamaterial applications.

The optical conductivity is a complex number, whose real part determines the loss in the 2D materials. Understanding the loss in 2D materials is important for applications such as photodetectors, where maximizing absorption is desirable. The real part is relatively easy to measure by transmission or reflection, as has been demonstrated in many previous works on graphene.^{11–13} On the other hand, the imaginary part of the optical conductivity is closely related to many important phenomena in optics. As an example, whether graphene supports transverse-electric (TE) or transverse-magnetic (TM) plasmons depends on the sign of the imaginary part of the optical conductivity.¹⁴ The imaginary part also determines the behavior of a hyperbolic

metamaterial consisting of truly 2D materials.⁹ However, obtaining the imaginary part is not as straightforward as the real part. In the case of graphene, most easily measurable quantities are dominated by the real part, and the broadband optical response of graphene prevents the usefulness of Kramers-Kronig relations. As a result, more sophisticated techniques have been developed to obtain the complex optical conductivity. For example, Li *et al.* extract the complex optical conductivity of graphene by carefully measuring the reflection and transmission together with the help of an interference layer and electrostatic gating.¹⁵ However, such a technique requires additional fabrication steps, which is not always applicable to the general need of determining the complex optical conductivity of a 2D material.

In this paper, we develop a simple and robust technique based on spectroscopic ellipsometry to determine the complex optical conductivity of truly 2D materials. This technique is applied to mono- and bilayer chemical-vapor-deposited (CVD) graphene, obtaining measurements of the optical conductivity from ultraviolet to mid-infrared wavelengths (from 230 nm to 7 μ m). We also study how chemical doping with nitric acid modifies the optical conductivity.¹⁶ Our technique extracts the optical conductivity by fitting the ellipsometric measurement of a 2D material on a known transparent substrate. Spectroscopic ellipsometry has been used extensively to study graphene in many previous works.^{17–22} However, they have used a phenomenological approach that models graphene, just like any other bulk material, as a layer with a non-zero effective thickness and an effective refractive index. In contrast, we model a truly 2D material such as graphene as an infinitely thin sheet with a surface conductivity. Our approach allows a more direct connection to theoretical predictions in which the optical conductivity is derived from the surface current induced in the 2D crystal by light.^{4–6} We demonstrate measurements of the complex optical conductivity of graphene over a broad spectral range from ultraviolet to mid-infrared. The mid-infrared properties are particularly

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interesting since graphene has been shown to be a good material for mid-infrared plasmonics and metamaterials.^{23,24}

Spectroscopic ellipsometry acquires the ellipsometric angles Ψ and Δ over a range of wavelengths at several incident angles. Ψ and Δ are defined by $r_p/r_s = (\tan \Psi)e^{i\Delta}$, where r_p and r_s are the reflection coefficients for p and s light, respectively. Since ellipsometers acquire the ratio and phase difference between r_p and r_s , rather than the absolute values of either, the measurement is relatively robust and reproducible. The Ψ and Δ data are then used to obtain the optical properties by fitting to a model of the sample. Conventionally, a model is constructed for the sample consisting of a refractive index (with real and imaginary parts) and thickness of each layer in the sample; fitting the model to the data provides the parameters in the model. However, for a truly 2D material such as graphene, it is more physical to model the layer by an infinitely thin sheet with an in-plane sheet optical conductivity σ . In this paper, we consider only the in-plane response because the out-of-plane response of

graphene is relatively weak. If this infinitely thin sheet is sandwiched between medium 1 and medium 2, the reflection coefficients for s and p light can be derived by matching the boundary conditions of the Maxwell equations

$$r_s = \frac{k_{1z} - k_{2z} - \sigma\omega\mu_0}{k_{1z} + k_{2z} + \sigma\omega\mu_0}, \quad r_p = \frac{\varepsilon_1/k_{1z} - \varepsilon_2/k_{2z} - \sigma/\omega}{\varepsilon_1/k_{1z} + \varepsilon_2/k_{2z} + \sigma/\omega}, \quad (1)$$

where k_{1z} , k_{2z} are the out-of-plane wave vectors of light in medium 1 and medium 2, respectively; ε_1 , ε_2 are the permittivities of the two media. In an ellipsometric measurement of a 2D material, medium 1 and medium 2 are the air and the substrate. Ψ and Δ predicted by the model can therefore be calculated from Eq. (1) and the definition of $r_p/r_s = (\tan \Psi)e^{i\Delta}$. In this model, the real and imaginary parts of the optical conductivity σ are the unknown parameters of interest. The Marquardt-Levenberg algorithm is applied to extract the optical conductivity σ which minimizes the mean square error (MSE) between the measured data and the model-predicted values defined by

$$MSE = \sqrt{\frac{1}{3n - m} \sum_{i=1}^n [(N_i^{EXP} - N_i^{MOD})^2 + (C_i^{EXP} - C_i^{MOD})^2 + (S_i^{EXP} - S_i^{MOD})^2]} \times 1000. \quad (2)$$

Here, n equals the number of wavelengths multiplied by the number of incidence angles; m is the number of fitting parameters; $N_i = \cos(2\Psi_i)$; $C_i = \sin(2\Psi_i)\cos\Delta_i$; $S_i = \sin(2\Psi_i)\sin\Delta_i$. The superscripts of *EXP* and *MOD* correspond to measured and model-predicted values, respectively. The subscript i indicates the particular set of data of a wavelength and an incident angle. The real and imaginary parts of the unknown optical conductivity σ as functions of wavelength are described by general smooth functions parameterized by cubic splines. The refractive index of the transparent substrate is described by the Sellmeier equation, whose coefficients are obtained from measurements of bare substrates.

We report here measurements of the optical conductivity of mono- and bilayer CVD graphene. The monolayer graphene is from Bluestone Global Tech (Gratom-M-Cu); Bilayer CVD graphene is grown by using the method reported in our previous paper.²⁵ Graphene samples are transferred onto CaF_2 substrates, which are transparent from ultraviolet to mid-infrared. Because the substrates have no absorption at the wavelengths of interest, Δ from the bare substrates is either 0 or π . Any deviation from 0 or π can be unambiguously attributed to graphene, which aids the robustness of the optical conductivity extraction.¹⁷ This method of using transparent substrates allows better extraction over a broad spectral range as long as the substrate maintains its transparency, while other contrast improvement methods such as interference enhancement can only work in a narrow spectral range.²⁰ The substrates are wedged by 2° to avoid backside reflection. To acquire data over a broader spectral range, we use two ellipsometers, Woollam M-2000 and Woollam IR-VASE, for wavelengths of 0.23 to 1.64 μm and 1.8 to 7 μm , respectively. The longest wavelength is limited by the choice of CaF_2 substrates, which start to have some

absorption at 8 μm . The angles of incidence used in the experiment are 47° , 57° , and 67° . The spot size of M-2000 is about 3 mm by 5.5 mm at 57° . We mask the samples for IR-VASE measurement because its spot size (8 mm by 20 mm at 57°) is larger than the graphene sample area (~ 10 mm by 10 mm). Bare CaF_2 substrates are measured and fitted by the Sellmeier equation to obtain the refractive index of CaF_2 .

Fig. 1(a) shows the optical conductivity of monolayer CVD graphene extracted by our technique. The quality of the fit can be quantified by the MSE defined by Eq. (2). The MSEs of the M-2000 and the IR-VASE measurements of the data shown in Fig. 1(a) are 0.88 and 4.65, respectively, indicating

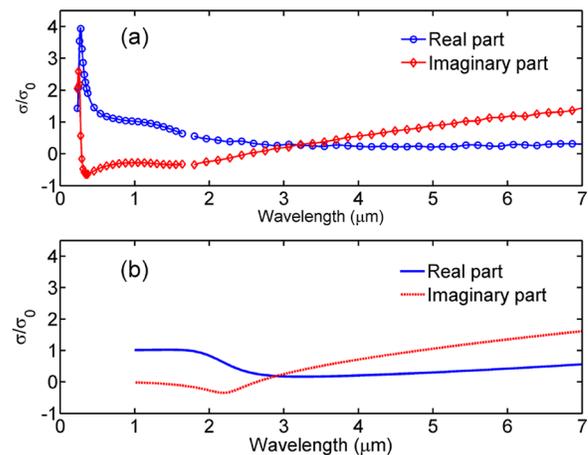


FIG. 1. (a) The extracted optical conductivity of a monolayer CVD graphene sample. (b) The optical conductivity of monolayer graphene predicted by the non-interacting theory with a Fermi level of 277 meV and a scattering rate (in units of energy) of 54 meV. The optical conductivity is normalized to the universal conductivity. The circles and diamonds are the control points of the cubic splines.

good fitting quality. As shown in Fig. 1(a), we observe a value of the optical conductivity very close to the universal conductivity of graphene around $1\ \mu\text{m}$. Also, the real part peak at 270 nm (with a photon energy of 4.6 eV) associated with the exciton-shifted van Hove singularity is observed. These results are consistent with previous reports.^{11,12,17,26} Notably, we obtain both the real and imaginary parts of the optical conductivity, while most previous works measure only the real part. To understand the measured conductivity, we plot in the Fig. 1(b) the theoretical conductivity curves predicted by non-interacting linear response theory⁴⁻⁶

$$\begin{aligned} \sigma(\omega) = & \frac{\sigma_0}{2} \left(\tan h \frac{\hbar\omega + 2\mu}{4k_B T} + \tan h \frac{\hbar\omega - 2\mu}{4k_B T} \right) \\ & - i \frac{\sigma_0}{2\pi} \log \left[\frac{(\hbar\omega + 2\mu)^2}{(\hbar\omega - 2\mu)^2 + (2k_B T)^2} \right] \\ & + i \frac{4\sigma_0}{\pi} \frac{\mu}{\hbar\omega + i\hbar\gamma}. \end{aligned} \quad (3)$$

In Eq. (3), the first two terms and the third term are contributed by the interband and the intraband transition, respectively. σ_0 is the universal conductivity defined by $e^2/(4\hbar)$; μ is the Fermi level; γ is the intraband scattering rate. Fig. 1(b) is plotted with a Fermi level of 277 meV and a $\hbar\gamma$ value of 54 meV, which provide the closest fit to the measured optical conductivity. We plot only the infrared wavelengths, since the theory within the independent-particle picture does not work well in the ultraviolet to visible range, where many-body corrections are required.^{11,17,27} It should be noted that although the theory reproduces the main features of the measured optical conductivity, some details are different. The measured conductivity shows a smoother feature around $2\ \mu\text{m}$ than the theoretical curves. A possible explanation is a non-uniform distribution of the Fermi level and scattering rate within the measuring spot size, which is supported by our measurements (not shown) with 10 times smaller spot size by using a focusing accessory of the ellipsometer. It is also possible to attribute part of the broadening to the damping in the interband transition, which is not included in the theoretical conductivity described by Eq. (3).

In Figure 2, we plot the extracted optical conductivity of mono- and bilayer CVD graphene versus photon energy. As expected for bilayer graphene, the real part of the conductivity approaches twice the universal conductivity for near-infrared photon energies. Notably, the peak in the real part of the conductivity of bilayer graphene is at 4.4 eV, which is red-shifted from the 4.6 eV peak of monolayer graphene. The observed red shift of the exciton-shifted van Hove singularity is consistent with reported measurements and first-principle calculations for bilayer graphene.^{11,27} In addition, the bilayer graphene shows a small peak at 0.4 eV in the real part of the conductivity, as indicated by the arrow in Fig. 2(b). This peak, associated with the interlayer coupling energy, has been observed in exfoliated bilayer graphene in the literature.^{11,28,29} Compared with the reported exfoliated bilayer graphene results, the peak we see in CVD bilayer graphene is less pronounced.

The samples corresponding to Figures 1 and 2 are unintentionally p-doped by the environment. The technique

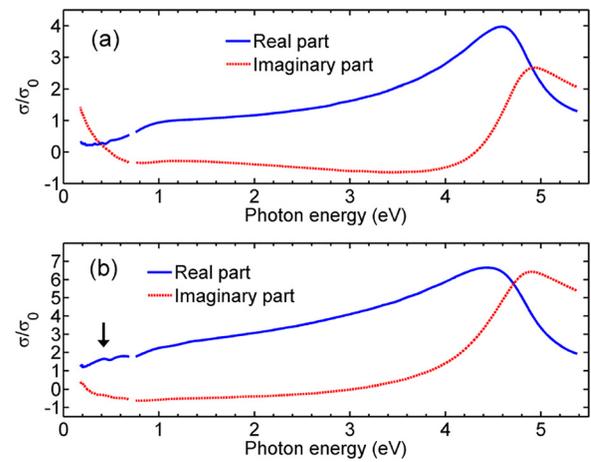


FIG. 2. (a) The extracted optical conductivity of a monolayer CVD graphene sample. (b) The extracted optical conductivity of a bilayer CVD graphene sample. The optical conductivity is normalized to the universal conductivity. The arrow in part (b) indicates the peak at 0.4 eV associated with the interlayer coupling energy of bilayer graphene.

developed in this paper is also applied to study how chemical doping modifies the optical conductivity. Chemical doping is performed by placing the sample in a container with nitric acid vapor for 15 min.¹⁶ The sample is then washed to remove excess nitric acid on the graphene surface. Figure 3 shows the optical conductivity of monolayer graphene before and after chemical doping by nitric acid vapor. According to the theoretical conductivity described by Eq. (3), the Fermi level can be identified by the local minimum of the imaginary part.¹⁵ The nitric acid chemical doping therefore pushes the Fermi level to -530 meV (relative to the Dirac point), as the imaginary-part local minimum at the wavelength of $1.16\ \mu\text{m}$ corresponds to a photon energy of twice the Fermi level. The real part in the near-infrared region is also decreased by Pauli blocking. On the other hand, the optical conductivity at wavelengths below $0.6\ \mu\text{m}$ shows negligible change. Although it has been reported that doping can modify the position and the shape of the exciton-shifted van Hove singularity peak, our doping change is not as strong as electrolyte gating to see this effect clearly.³⁰

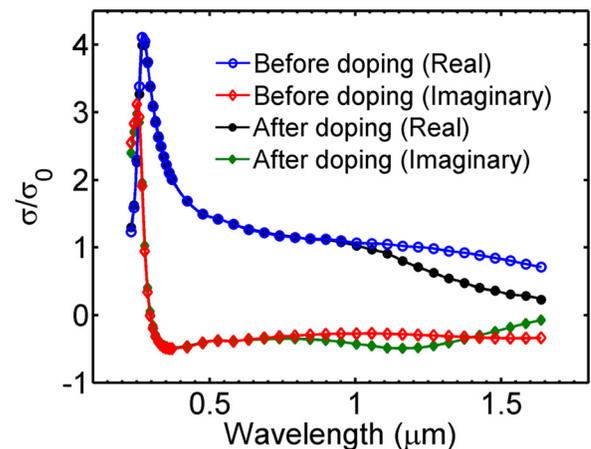


FIG. 3. The extracted optical conductivity of a monolayer CVD graphene sample before and after chemical doping by nitric acid vapor. The optical conductivity is normalized to the universal conductivity. The markers are the control points of the cubic splines.

In summary, we have demonstrated a technique that extracts the complex optical conductivity of mono- and bilayer CVD graphene by spectroscopic ellipsometry. In our technique, graphene is modeled as a truly 2D material, which is in contrast to the phenomenological modeling using an effective index and effective thickness as in previous work. We obtain the experimental optical conductivities of mono- and bilayer CVD graphene over a broad spectrum from ultraviolet to mid-infrared and study how chemical doping modifies the optical conductivity. We expect that this method will become increasingly important as more 2D materials are developed for optoelectronics and metamaterial applications, where both the real and imaginary parts of the conductivity are important.

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