

Optical Conductivity of Single Layer Graphene from Experimental Measurements and Theoretical Calculations

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Abstract: With the fast growing research and applications of graphene in photonics, understanding its properties and their correlation over broad spectral range is essential. The study presented herein is an analysis of optical conductivity and absorbance of chemical vapour deposition (CVD) single layer graphene (SLG). Optical transmittance measurements of the SLG module were performed over photon energy range from near-ultraviolet (NUV, 300 nm) to near-infrared (NIR, 2500 nm) spectral regions. For photon wavelengths between 380 and 750 nm, graphene yielded an average transmittance of 97.6% with a maximum transpance peak of 98.3% at 710 nm wavelength. These results compares favorably with the reported theoretical $T(\omega)$ of 97.7%. Arguably, the numerical value of optical conductivity, σ for SLG (expressed in terms of universal optical conductivity, σ_o), equates to the absorbance (in units of $\pi\alpha$). Within the visible region, $\sigma / \sigma_o = 1.04$, which shows a close approximation of σ to σ_o . However, within the NIR and NUV, this approximation of σ disappears, where its value decreases sharply with energy in the NUV region. This behavior of the optical conductivity approximating to the universal optical conductivity may be explained in terms of the contributions from inter-band and intra-band transitions.

Keywords: Band transitions, optical absorbance, optical conductivity, single layer graphene

I. Introduction

Graphene is an atomically thin, two-dimensional (2D) carbon material with fascinating optoelectronic properties arising from its zero-energy band gap electronic structure [1]. Electrons through the material hop with minimal scattering and at very high velocity (Fermi velocity) of $\sim 1 \times 10^6 \text{ m/s}$ [2]. The electronic properties of graphene exhibit linear dispersion of energy and momentum near the Fermi energy and therefore can be modeled in terms of relativistic massless Dirac Fermions [3]. Light-matter interaction in graphene is predicted to exhibit a simple optical absorption spectrum in the Vis-to-IR spectral range and with an absorbance of $\pi\alpha = 2.3\%$ independent of frequency [4-7], where $\alpha = e^2/\hbar c \approx 1/137$ is the fine structure constant, \hbar is the reduced Planck's constant and c is the finite speed of light. The universal absorbance of graphene is equivalent to frequency-independent optical sheet conductivity given by, $\sigma_o = \pi e^2/2h$ [8].

Previous studies have suggested that the optical sheet conductivity of graphene arises from chiral resonance in which, upon absorption of a light photon, a particle-antiparticle pair is created [9].

The optical conductance of SLG is defined by the sum of the contributions of the intra-band ($\pi - \pi^*$) and inter-band ($\sigma - \sigma^*$) transitions (Equation 1) [10, 12]:

$$\sigma = \sigma_{\pi-\pi^*} + \sigma_{\sigma-\sigma^*} \quad (1)$$

These transitions can be represented as shown in figure 1. The $\sigma - \sigma^*$ transitions are high energy transitions involving short wavelengths ($< 150 \text{ nm}$) and do not fall in the UV-Vis range, while the $\pi - \pi^*$ are low energy transitions occurring in the UV-Vis region hence can be observed.

For the $\pi - \pi^*$ transitions, optical conductance can be represented as a complex number (Equation 2):

$$\sigma_{\pi-\pi^*} = \sigma_r + i\sigma_i \quad (2)$$

Where σ_r and σ_i represent the real and imaginary optical conductance of graphene modeled using theoretical conductivity curves predicted by non-interacting linear response theory [12, 13].

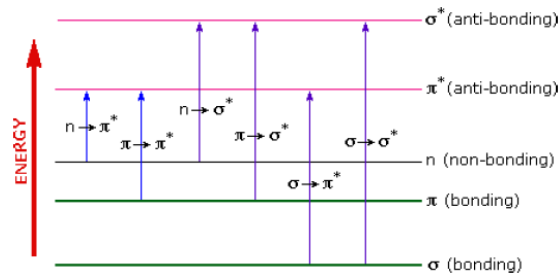


Figure 1: Intra-band and inter-band transitions at different energy levels [11]

For incident photon of $\lambda = 550 \text{ nm}$ at room temperature ($T = 300\text{K}$), σ_r and σ_i have been estimated to be $\sigma_r = 1.016\sigma_0$ and $\sigma_i \approx 0$ hence $\sigma_{\pi-\pi^*} \approx \sigma_0$ [12]. Further reports also indicate that, the energy gap between $\sigma - \sigma^*$ bands is $\approx 6 \text{ eV}$ [14]. Since this energy gap is larger than the energies of the photons in the visible range, the $\sigma - \sigma^*$ transitions majorly result in a phase shift of optical waves that pass through the graphene sample and thus contribute only to dispersion. And since the thickness of few layer graphene (FLG) is much smaller than the wavelength of the incident photons in the visible range, the phase shift observed is usually minimal and therefore negligibly treated [14, 15]. The relation between transmittance $T(\omega)$ and the optical conductivity $\sigma(\omega)$ for SLG [8, 16-18] is given by:

$$T(\omega) = (1 + 2\pi\sigma_1(\omega) / c)^{-2} \tag{3}$$

Equation (3) can also be expressed as:

$$T(\omega) = \left(1 - \frac{4\pi}{c} \sigma_1(\omega)\right) \tag{4}$$

which upon rearrangement translates to:

$$\sigma_1 = (1 - T(\omega)) \frac{c}{4\pi} \tag{5}$$

where, $1 - T(\omega) = A (\approx \pi \alpha)$ is the absorbance [12, 19].

From the UV-Vis-NIR spectrophotometer measurements [20, 21], optical absorbance (A) is related to the transmittance (T) and reflectance (R) data by the expression:

$$A = 1 - T - R \tag{6}$$

Therefore, optical conductivity $\sigma_1(\omega)$ of SLG [10] can be expressed as:

$$\sigma_1(\omega) = A \frac{c}{4\pi} \tag{7}$$

This optical conductivity ($\sigma_1(\omega) = \sigma$) can also be expressed in terms of the universal optical conductivity, which takes form of a ratio as given by Equation (8):

$$\frac{\sigma}{\sigma_0} = \left(A \frac{c}{4\pi}\right) / \left(\frac{\pi e^2}{2h}\right) \tag{8}$$

This gives:

$$\begin{aligned} \frac{\sigma}{\sigma_0} &= \left(\frac{c}{4\pi}\right) \left(\frac{2h}{\pi e^2}\right) A \quad \text{or} \\ \frac{\sigma}{\sigma_0} &= \frac{1}{\pi} \left(\frac{hc}{2\pi e^2}\right) A \end{aligned} \tag{9}$$

In this work, analysis of optical conductivity for CVD grown SLG, in the spectral range from NUV (300 – 380 nm) [22] through the Vis (380 - 750 nm) to NIR (750 - 2500 nm) [23] regions is reported. We show that, within the visible range, the σ approaches the universal conductivity. In the extremes of NIR and NUV, the optical conductivity is minimal. This study is aimed at advancing the novel photonics and optoelectronics applications of SLG and its derivatives.

II. Materials and methods

Single layer graphene module (#Y060515, USA) synthesized through chemical vapour deposition (CVD) and transferred on Fluorine-doped Tin Oxide (FTO) substrate via poly(methyl methacrylate) (PMMA) technique was used. The thicknesses and quality of the SLG samples were determined using Raman Spectroscopy (Renishaw Ramascope) [1]. Investigation of optical properties was done using UV-Vis-NIR spectrophotometer (*SolidSpec 3700*). Transmission and reflection spectra were measured and analyzed between 300 - 2500 nm in 1 nm steps. From the spectrophotometer, optical transmittance, T(%) and reflectance R(%) of bare FTO substrate and of the SLG on FTO (SLG/FTO) were obtained and recorded.

III. Results and discussion

Our spectrophotometer measurements for the optical transmittance, T(%) plotted against wavelength from NUV to NIR spectral region are as shown in Figure 2. The spectra for both SLG/FTO and bare FTO show a very high transparency within the visible and NIR spectral regions. The transmittance of SLG/FTO reached a value of 76.7% in the visible domain, which is very functional for photovoltaic applications. Towards the NUV region, it dropped significantly with the value reaching zero in the NIR at lowest energy. This is in agreement with the results reported by Kim et al. [24].

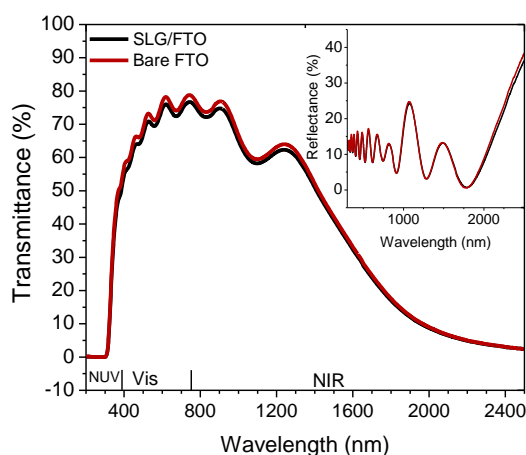


Figure 2: Measured transmittance spectra of bare FTO substrate and SLG/FTO vs. wavelength from NUV to NIR spectral region showing high transmittance occurring within the visible and NIR region. Inset: corresponding reflectance (%) spectra.

Using equation (5), the absorbance, A(%) of SLG was determined from the difference between the absorbance of FTO and SLG/FTO. This absorbance was plotted against energy within the NIR (0.50 - 1.66 eV), Visible (1.66 - 3.27 eV), and NUV (3.27 - 4.14 eV) spectral regions as shown in Figure 3.

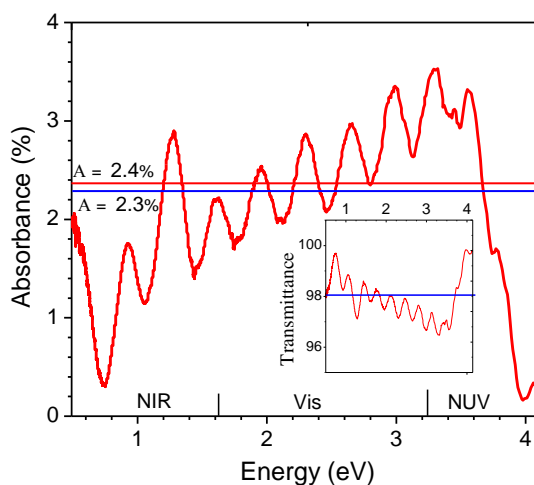


Figure 3: Optical absorption spectra SLG from NIR to NUV energy region showing an absorbance of 2.4% (red line) in visible spectrum slightly above the theoretical opacity of 2.3% ($\pi\alpha$) (blue line). Inset: Optical transmittance profile for the SLG sample with transmittance of 98.3% in the visible region.

The optical absorbance was found to increase with energy. Specifically, within the NIR region, absorbance has a maximum absorption peak of 2.9% at 1.28 eV and 3.5% in the visible region where the average absorbance is 2.4%, a value slightly higher than the reported value of 2.3% [4-7]. Within the NUV region, absorbance decreased from 3.5% peak to almost zero towards the high-energy region (at 4.14 eV). Moreover, optical absorption within the spectrum was dominated by constant peak fluctuations especially in the visible region. This higher absorption of 2.4% in the visible region and the observed peak fluctuations can be attributed partly to surface contamination of the samples during the experiments and partly to apparatus signal-to-noise ratio, which was somehow high over the whole spectrum.

According to equation (9), a plot of the optical conductivity expressed in terms of the universal optical conductivity, σ / σ_o (Figure 4) generally increases with photon energy within the spectrum. In the low energy region (NIR), $\sigma / \sigma_o < 1$ at an average value of 0.62, while for the visible region, the average value is 1.04. However, within the NUV region, this value increased to a peak of 1.54 at ~3.3 eV, then dropped sharply. Generally, for SLGs, σ / σ_o is reported to increase with photon energy [13, 25-27].

To understand the trends in optical absorbance (Figure 3), we related the optical conductivity in units of universal conductivity (equation 8) to the optical absorbance in units of $\pi\alpha$.

Since $\frac{hc}{2\pi e^2} = \frac{1}{\alpha}$

Thus, equation (9) can be expressed as:

$$\frac{\sigma}{\sigma_o} = \left(\frac{1}{\pi\alpha} \right) A \tag{10}$$

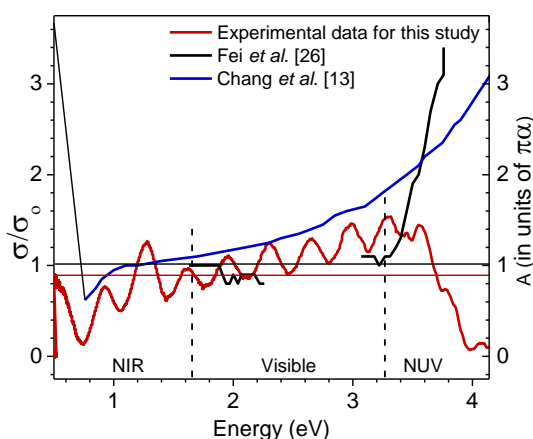


Figure 4: A comparison of optical conductivity, σ / σ_o and absorbance of SLG as a function of photon energy from NIR to NUV using our experimental data (red), extracted data Fei et al. [26] (black) and Chang et al. [13] (blue). Within the visible range, the value of $\sigma / \sigma_o \approx 1$. The right scale shows that the absorbance of SLG in units of $\pi\alpha$ is in the same range as the optical conductivity in terms of the universal optical conductivity.

Within the visible region, our SLG experimental optical conductivity value was 1.04 and compares to the reported value of 0.9 [26]. Since the absorption coefficient of SLG is proportional to σ within the visible region, its universality is in agreement with the theoretical expectations where, $\sigma / \sigma_o \approx 1$ as reported [8, 12, 18]. This universality has been associated to the existence of density of states (DOS) as discussed extensively [26, 27] and ceases beyond the visible region where σ / σ_o increases rapidly [26]. Our results, however, show a decrease in σ / σ_o to almost zero in NUV region hence showing non-universality of σ . This may be contributed by the intra-band transitions.

IV. Conclusion

In summary, we provide that, UV-Vis-NIR spectrophotometer is valid for studying graphene and determining its optical conductivity. When σ is expressed in terms of universal optical conductivity, σ_o , its numerical value is equivalent to the optical absorbance value (in units of $\pi\alpha$). By comparing our experimental results for optical conductivity and theoretically values, we show that, in the visible region, universality of σ exists with $\sigma \approx \pi\alpha$. Within the NIR and NUV region, the universality of σ disappears. This work reveals more aspects of graphene optical properties, and gives inspiration for more effective detection and analysis of graphene in the IR and UV region.

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