Preliminary Studies on the Reflectance Characteristics of graphene/SiO₂ under Different Applied Voltages for Optical Modulation Applications

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Abstract. A preliminary study on the interband transition of graphene was done via reflectance spectra of graphene/SiO₂ sample at various applied potential. Prior to that, Raman spectroscopy and four-point probe measurement was done on graphene/SiO₂ sample. It was found that the sample consisted of monolayer graphene with sheet resistance around 402.32 Ω/□. Post-processing of the reflectance data lead to the plot of ratio of change in reflectance towards reflectance at 0 V (ΔR/R) against applied potential. From there, the ratio increases along with applied potential, indicative of higher absorption due to interband transition.

1. Introduction
Graphene in general described either mono- or multilayer of sp²-hybridized carbon atoms arranged in a honeycomb network along a two dimensional (2D) plane. Graphene possessed many unique characteristics such as high optical transparency, electrical and thermal conductivity, which is essential in many applications such as smart touch screens and thermal management [1-3].

Aside from that, graphene is widely studied in the realm of photonics due to its strong electro-optic effects [4-6]. Optical devices and application such as optical modulator, terahertz wavelength emitter/detector, and electrochromic devices often required the utilization of graphene material [7, 8]. The electro-optic effect of graphene originated from its unique band structure, i.e. two symmetrical cones with vertices met at the Dirac point [9]. In addition, the Fermi level (E_F) of pristine graphene also coincided at the Dirac point [6, 9]. This enabled interband transition, a feature present in most semiconductor material to occur. Furthermore, the 0 eV bandgap of graphene implied absorption over a majority of the broad electromagnetic (EM) spectrum [6, 10-12].

The interband transition in graphene at E_F = 0 eV is mostly responsible for the broad optical absorption. Should interband transition been interrupted, e.g. blocked at a designated EM spectrum, graphene thus become transparent. The manipulation of interband transition could be achieved through many methods, such as optical and electrical. Between them, the latter was easier to implement due to matured CMOS technology [13]. By applying an external voltage, the Fermi level of graphene varies. Interband transition of graphene thus rendered forbidden via Pauli blocking when photon energy, hν≤2E_F [6, 12, 14]. This also indicative of graphene become transparent up to 2E_F [6, 12, 14].

The phenomena of interband transition and Pauli blocking via external voltage bias is often utilized in the fabrication of optical modulator. In this work, the reflectance spectra of graphene/SiO₂ at different applied potential was used to investigate the relation between interband transition and applied potential. Prior to that, Raman spectroscopy, as well as four-point probe measurements were
performed in order to identify the characteristics such as graphene layers and electrical conductivity of the samples.

2. Methodology

In this work, commercially purchased graphene on SiO$_2$/Si substrate (grown using CVD method, sample denoted as graphene/SiO$_2$) was used. Raman measurement (Jobin Yvon HR 800) was performed using an Ar$^+$ laser source at 514.5 nm, operates at 20 mW. Next, the average resistance of graphene/SiO$_2$, subsequently resistivity have been determined by four-point probe analysis. There, a 4 × 1 berg strip, spaced at 2.54 mm each, was used to mount the pogo pins that served as probes. Electrical connections were established by connecting one end of the berg strip towards a Keithley 2400 Source Measurement Unit (SMU). Based on the principles of four-point probe measurement, electrical current would be sourced and the corresponding voltage would be measured. From there, an I-V curve was obtained.

The as-received graphene/SiO$_2$ was measured of its reflectance using UV-Vis-NIR spectrometer (Agilent, Cary 5000). Next, the sample was reconfigured with external wirings that would be connected to a direct current (dc) voltage supply. The sample was remounted into the UV-Vis-NIR system, and several reflectance measurements were performed at voltages ranging from 0 to 30 V, with 5 V intervals.

3. Results and Discussion

3.1 Raman Spectroscopy of graphene/SiO$_2$

![Figure 1. Raman spectrum of graphene/SiO$_2$.](image-url)
Raman spectroscopy is widely used to determine the characteristics of graphene such as defect levels, domain size, and number of graphene layers. Figure 1 shows the Raman spectrum of the graphene/SiO$_2$. From there, two notable bands centered ~1600 and 2696 cm$^{-1}$ were noted, which signified the G and 2D bands of graphene [15]. The weak D band (~1354 cm$^{-1}$) indicative of low level of defects, hence the corresponding graphene sample is of high quality. Since the relative intensity ratio between G and D bands were very high, the graphene domain size can be calculated using Tuinstra-Koenig relation [16]:

\[ L_a (nm) = (2.4 \times 10^{-10}) \times \lambda^4 \times \left( \frac{I_D}{I_G} \right)^{-1} \]  

(1)

Where $L_a$ is the average graphene domain size, $\lambda$ is the incident wavelength (514.5 nm in this study); $I_G/I_D$ is the relative intensity ratio between G and D band. $L_a$ was found to be ~1.81 $\mu$m.

On the other hand, the attributes of 2D band was suited for determining the number of graphene layers. In general, the relative intensity ratio between 2D and G, denoted as $I_{2D}/I_G$, would be a more parameter describing the aforementioned [17]. For monolayer, $I_{2D}/I_G >> 1$; while $I_{2D}/I_G \sim 1$ corresponded to bilayer. As $I_{2D}/I_G < 1$, the presence of 3 layers or above were guaranteed [17]. Here, $I_{2D}/I_G \sim 1$, which indicative of bilayer graphene at glance. However, when other factors e.g. full-width at half maximum (FWHM) of 2D (~30 cm$^{-1}$), and the distinct narrow G* band taken into account, monolayer graphene were to be expected instead.

3.2 I-V characteristics of graphene/SiO$_2$

![Figure 2. I-V characteristics of graphene/SiO$_2$.](image)
The I-V characteristics of graphene/SiO$_2$ is plotted and shown in Figure 2. Since the I-V curve obtained from four-wire measurement as a consequence of four-point probe configuration, instead of voltage, a range of current was introduced. Hence, the vertical axis represented voltage while that of current at horizontal. From there, a linear trend was observed. Based on the plot, the sheet resistance, $R_s$, of graphene/SiO$_2$ could be calculated using the following expression [18, 19]:

$$R_s = \frac{\pi}{\ln 2} \frac{V}{I}$$

(2)

Where $V/I$ is the gradient of the I-V plot. The $R_s$ of graphene/SiO$_2$ calculated was 402.32 Ω/□. This result is comparable to those reported in literature [20].

3.3 UV-Vis-IR Reflectance of graphene/SiO$_2$ under the effects of applied potential

![Figure 3. Reflectance spectrum of graphene/SiO$_2$ at 0 V.](image)

The high electrical conductivity of graphene allowed its optical characteristics to be manipulated in the presence of an electric field. With reference to 0 V biased sample, a reflectance spectrum was plotted and shown in Figure 3. From there, two regions with distinct features were identified. In this
work, the graphene is placed on top of SiO$_2$/Si, resulting in a three layer system, i.e. graphene/SiO$_2$/Si (Si was omitted in most discussions since it served as a substrate). In general, for any UV-Vis-NIR measurements, the relation (as a function of photon frequency $\omega$), among absorption $A(\omega)$, transmittance $T(\omega)$, and reflectance $R(\omega)$ can be described as [21]:

$$A(\omega) + T(\omega) + R(\omega) = 1$$

(3)

At region A, Si was opaque, thus maximizing light reflection. The oscillating pattern could be ascribed to interference of reflected light from polished Si substrate transmitting through SiO$_2$ (estimated thickness ~300nm). Given that the thickness of SiO$_2$ far greater than that of graphene (0.35 nm for monolayer), which lead to strong oscillations, further analysis in this region was inhibited.

On region B, IR light source partially transmitted into Si given its reduced opacity in that region. Since light reflected from certain depth of Si substrate, a rather flat band was observed in lieu of oscillating patterns. A wavelength of 1550 nm would be chosen for further analysis for the rest of the spectra. The wavelength of 1550 nm, also known as C-band, is often used in optical communication applications.

![Figure 4. Plot of ($\Delta R/R$) against applied voltage.](image)

In order to exclude the contributions of SiO$_2$/Si from graphene/SiO$_2$/Si system, the subsequent reflectance plots, i.e. applied voltage > 0V (denoted as $R_{V \geq 1}$), would be subtracted and a ratio with respect to that of 0 V ($R_{V=0}$). Hence,
\[ \frac{\Delta R}{R} = \frac{|R_{y=0} - R_{y>1}|}{R_{y=0}} \]  

Figure 4 shows the changed in reflectance at 1550 nm for graphene/SiO\(_2\) samples under different potential difference. An overall increasing trend in term of \(\Delta R/R\) was observed, which signified voltage biased graphene yield lesser reflectance. By excluding the effects from absorption, transmittance, and reflectance from both SiO\(_2\) and Si substrate, the changes observed in \(\Delta R/R\) could be attributed to the absorption of graphene.

The absorption of monolayer graphene was expressed as \(\pi \alpha = 2.3\%\), where \(\alpha\) is the fine structure constant [6]. This implied the optical absorption of monolayer graphene saturated at \(\sim 2.3\%\). However, the behaviour of \(\Delta R/R\) suggested the absorption of graphene increases along with applied voltage. One plausible reasoning would be the overall absorption of graphene was less than the theoretical predicted value due to effects from SiO\(_2\), which lowers the overall absorption [21]. Graphene is known to be sensitive towards various factors such as interfacial material that would lead to unintentional doping. In case for SiO\(_2\), the optical transition of graphene/SiO\(_2\) would be lesser since the Fermi level of graphene was shifted towards the valence band. This promotes intraband conduction where graphene become transparent [14]. As an external field, i.e. voltage was introduced, the Fermi level of graphene shifted towards the Dirac point, favouring interband transition [6, 12, 14]. The inherently increases the absorption of graphene.

4. Conclusions
The commercially purchased graphene/SiO\(_2\) consisted of monolayer as evident from Raman measurements. Four-point probe analysis indicated that the sheet resistance of graphene about 402.32 \(\Omega/\Box\). The reflectance spectrum of pristine graphene/SiO\(_2\) revealed two distinct regions, in which the region of interest fell in the IR range. The behaviour of \(\Delta R/R\) plot suggested lesser absorption of graphene compared to theoretical value due to intraband transition. Interband transition would be favoured over that of intraband in the presence of external electric field, which shifted the Fermi Level from the valence band towards the conduction band.

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