Gate-Controlled Nonlinear Conductivity of Dirac Fermion in Graphene Field-Effect Transistors Measured by Terahertz Time-Domain Spectroscopy

Inhee Maeng,†∥ Seongchu Lim,‡∥ Seung Jin Chae,‡ Young Hee Lee,*‡‡ Hyunyong Choi,§ and Joo-Hiuk Son*†

†Department of Physics, University of Seoul, Seoul 130-743, Korea
‡Department of Physics, Department of Energy Science, Sungkyunkwan Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon 440-746, Korea
§School of Electrical and Electronic Engineering, Yonsei University, Seoul 120-749, Korea

Supporting Information

ABSTRACT: We present terahertz spectroscopic measurements of Dirac fermion dynamics from a large-scale graphene that was grown by chemical vapor deposition and on which carrier density was modulated by electrostatic and chemical doping. The measured frequency-dependent optical sheet conductivity of graphene shows electron-density-dependence characteristics, which can be understood by a simple Drude model. In a low carrier density regime, the optical sheet conductivity of graphene is constant regardless of the applied gate voltage, but in a high carrier density regime, it has nonlinear behavior with respect to the applied gate voltage. Chemical doping using viologen was found to be efficient in controlling the equilibrium Fermi level without sacrificing the unique carrier dynamics of graphene.

KEYWORDS: Graphene, THz-time domain spectroscopy, optical conductivity, scattering time, intraband transition

Graphene is composed of carbon atoms in a two-dimensional hexagonal lattice structure. It has a band structure that is linearly dispersed with respect to momentum. Its exotic physical phenomena such as massless Dirac particles, room-temperature quantum Hall effect, and micrometer-long mean free path are of great interest in many fundamental science areas.1–6 The long mean free path and massless carrier of graphene give rise to its high carrier mobility exceeding 200 000 cm²/V·s, which has led to worldwide research into its applicability in high-speed electronics.7–11 Recently, the incorporation of a few 10 nm of graphene into source–drain electrodes has led to a graphene field effect transistor (FET) with a cutoff frequency of a few hundred gigahertz.8

The integration of graphene into electronic devices requires precise control of the channel carriers. Researchers have considered using organic molecules, alkali metals, or gas-phase doping during the chemical vapor deposition (CVD) process to modulate the majority carriers and the carrier concentrations.12–14 In the case of organic molecules and alkali metals, the doping agent adsorbed on the graphene invokes a transfer of charges depending on the relative position of the Fermi level. The doping is expected to perturb the electrical conductivity, carrier mobility, and relaxation time. Therefore, the analysis of the graphene carrier dynamics is as important as its static counterpart in the application of graphene to radio frequency circuits, photodetectors, optical modulators, and voltage amplifiers.15–17

Previous studies have used optical characterizations to understand the carrier dynamics of graphene.18–22 In those studies, the difference between transmitted and reflected optical outputs from graphene layers was used to analyze the changes in the electrical properties of the graphene that is susceptible to the environment. Interestingly, these optical signals are more sensitive to electronic structures from the infrared to terahertz range rather than to the optical range.21 In particular, using terahertz as a probing beam allows us to characterize the carrier dynamics near the Fermi level because of the small excitation energy.

In this paper, we present the direct terahertz time-domain spectroscopic (THz-TDS) measurement of CVD-grown graphene, whose carrier density was modulated by either a gate bias or an organic dopant. Our results imply that the carrier dynamics of gate-modulated graphene can be understood within the context of the Drude model; at a low carrier density, the optical conductivity of graphene is constant regardless of the applied gate voltage, but in a high carrier density regime, it has nonlinear behavior with respect to the applied gate voltage. Chemical doping using viologen was found to be efficient in controlling the equilibrium Fermi level without sacrificing the unique carrier dynamics of graphene.

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density, \(N(\sigma(\omega) \sim \sqrt{N})\). In the case of chemical doping with viologen, the Dirac point significantly shifted from 40 V to near 0 V. Nevertheless, the Drude-like carrier properties were retained, and the carrier properties were only slightly changed.

Monolayer graphene was synthesized on Cu foil inside a CVD chamber. The detailed growth conditions have been described elsewhere including the dependence on the temperature, pressure, time, and hydrocarbon gas. After the synthesis, the underlying Cu foil was removed using metal etchant. The graphene was then rinsed with deionized water several times and was transferred onto Si substrate with a 300 nm thick SiO\(_2\) layer. As shown in the Supporting Information, we confirmed that the transferred graphene was a monolayer via Raman spectroscopy, transmission electron microscopy, and a selected-area electron diffraction pattern. To observe the carrier dynamics in the THz region as a function of the carrier concentration, source and drain electrodes were made on the graphene using a silver paste. A heavily B-doped Si substrate (1–10 \(\Omega\)-cm) was used as a gate electrode, as shown schematically in Figure 1a. Gate bias was applied between the Si back gate and the source electrode. The channel of our graphene FET was square with an area of 6 \(\times\) 6 mm\(^2\). Its morphological image is shown in the inset of Figure 1a, revealing a series of ripples. As an alternative to the electrostatic doping using gate bias, an organic dopant was used. Since the CVD-grown graphene has p-type behavior in air, we used a strong n-type dopant, viologen. The preparation of viologen has been well described in the literature. One milliliter of viologen-containing toluene was dropped on the sample. It was then spin-coated at 2000 rpm for 1 min and dried until the toluene was completely evaporated.

Our THz-TDS system has been described elsewhere. To minimize THz absorption by water molecules in air, our system was kept inside a chamber that held the humidity level below 3%. A blank Si substrate (a reference sample) and graphene FET were comparatively studied to eliminate the effect of the substrate. For instance, we mounted both the reference and the graphene FET on a computer-controlled linear stage, alternately exposing them through an aperture to a THz beam at a frequency of 0.5 Hz, and we took the differential of the THz transmission. This removed the absorption of THz by the substrate from the signal and allowed us to quantify the THz transmission by graphene FETs. Also, the modulation of the THz transmission was conducted at different gate voltages from -50 to 50 V with a 5 V step. The transmission at each gate bias was normalized by that of the zero gate bias.

The inset of Figure 1b shows the THz time-domain transmission amplitude of the graphene FET in the range 0.2–1.5 THz. In the zoomed-in view in Figure 1b, clear changes in the THz time-domain signals can be observed as a function of the applied gate voltage. The peak transmission of the graphene FET at zero gate voltage is around 94% of the reference signal. The maximum transmissions at gate biases of 45 V and -30 V approach 97 and 90%, respectively, of those of the reference. This indicates that the spectral amplitude is sensitive to the carrier density of the graphene channel. In the left panel of Figure 1c, the spectral transmission from 0.2 to 1.5 THz is further analyzed at three different gate voltages: 45, 5, and -20 V. The THz transmission amplitude became approximately constant over this range, although it decreased significantly as the gate voltage decreased from 45 to -20 V. The THz transmission of the graphene channel was investigated more systematically as a function of gate bias.

Figure 1. (a) Schematics of graphene FET and its AFM image on the graphene channel. (b) THz time-domain transmission amplitude of graphene FET (including 0.2–1.5 THz) in terms of applied gate voltage. The inset shows the entire time-domain transmission amplitude. (c) The left panel is the normalized frequency-dependent transmission of the THz signals with different gate voltages, and the right panel is an average gate-dependent THz transmission from 0.4 to 1 THz as a function of gate voltage.

The right panel of Figure 1c is an average transmission (from 0.4 to 1 THz) at each gate bias. The gate-dependent transmission curve exhibited a minimum transmission of 82% at -30 V, continuously increased to 93% at 20 V, and reached a maximum of 97% at 45 V. The maximum transmission occurred at the CNP, at which the carrier density of graphene is the smallest. This result indicates that the transmission of THz is primarily responsible for the carrier density, which can be precisely controlled using the gate bias.
The measured THz transmission of graphene FET was further analyzed to understand the change in the optical sheet conductivity \( \sigma \) of our graphene films, based on the formula describing the thin film transmission \( T \).\(^{(52)} \) Since the phase shifts of the time-domain THz are negligible, as can be seen in Figure 1b, the intraband conductivity can be described using only the real part of the conductivity

\[
\frac{\sigma(\omega)}{\sigma_Q} = \frac{8k_BT}{\pi\hbar}\ln(\frac{e^{\frac{E_F}{2k_BT}} + e^{\frac{E_F}{2k_BT}}}{1 + e^{\frac{E_F}{k_BT}}}) \propto T \quad \text{when} \quad k_BT \gg E_F, \text{low carrier density} \quad (\text{Eq. 2})
\]

\[
\frac{\sigma(\omega)}{\sigma_Q} = \frac{4E_F}{\pi\hbar}\left(\frac{1}{e^{\frac{E_F}{k_BT}} + \frac{1}{e^{\frac{E_F}{k_BT}}}}\right) \propto E_F \quad \text{when} \quad k_BT \ll E_F, \text{high carrier density} \quad (\text{Eq. 3})
\]

where \( E_{\text{sample}} \) and \( E_{\text{ref}} \) are the transmitted THz signals through the graphene and the reference, respectively. \( E_{\text{gate}} \) and \( E_{\text{gate0}} \) are the transmitted THz signal of graphene FET at a given and zero gate voltage, respectively. Therefore, the first term \( [E_{\text{gate}}(\omega)]/(E_{\text{gate0}}(\omega)) \) is the THz transmission normalized by the gate bias at 0 V. The second term \( [E_{\text{gate0}}(\omega)]/(E_{\text{ref}}(\omega)) \) is normalized by a blank substrate. \( n_{\text{ref}} = 3.4 \) is the refraction index of the substrate Si layer because the THz wavelength is sufficiently large compared to the thickness of the oxide layer, \( Z_0 \) is the vacuum impedance (376.7 \( \Omega \)), and \( d = 3.5 \) Å is the thickness of the graphene film. The measured optical sheet conductivities at three different gate voltages are shown in Figure 2a. The sheet conductivity was relatively flat in the frequency range from 0.4 to 1.0 THz, which implies a broadened spectral width of the Drude scattering. The inset shows a similar frequency response from another sample in the same frequency range.

The Drude model provides an intuitive framework for low-energy carrier dynamics during the modulation of optical conductivity by gate bias. Assuming a zero-gap nature of graphene, the full intraband conductivity is described as\(^{(28)} \)

\[
\frac{\sigma(\omega)}{\sigma_Q} = \frac{8k_BT}{\pi\hbar}\ln\left(\frac{e^{\frac{E_F}{2k_BT}} + e^{\frac{E_F}{2k_BT}}}{1 + e^{\frac{E_F}{k_BT}}}\right) \propto T \quad (\text{Eq. 1})
\]

where \( \sigma_Q \) is the quantum conductivity defined as \( \pi e^2/2h \) and \( E_F \) is the Fermi energy. \( \tau \) is the scattering time and \( v_F = 1.1 \times 10^6 \) m/s is the velocity of the Dirac fermions.\(^{(22,29)} \) However, depending on the carrier density, the above conductivity (normalized by the quantum conductivity \( \sigma_Q \)) can be further classified into the following two regimes:\(^{(30,59)} \)

\[
k_BT \gg E_F, \text{low carrier density} \quad (\text{Eq. 2})
\]

\[
k_BT \ll E_F, \text{high carrier density} \quad (\text{Eq. 3})
\]

The above intraband electrodynamics reveals the following two key facts. First, when the carrier density is low so that \( E_F \) is close to the Dirac point, the optical sheet conductivity depends only on the temperature and not the carrier density. Thus, with a low carrier density, the optical conductivity is expected to be constant unless the temperature changes. This is clearly shown in Figure 2b. Near the gate bias of 45 V, at the lowest optical sheet conductivity, \( E_F \) is located at the Dirac point, leaving the graphene neither electron- nor hole-rich. The optical conductivity remained constant since all of our measurements were taken at room temperature. This region is known as the puddle regime that the minimum electrical conductivity is attributed to impurities and trap charges. Second, when the carrier density is high like the gate bias below \(-25 \) V in Figure 2b, strong gate-voltage-dependent optical sheet conductivity was observed. In this regime, the governing carrier dynamics is dense-hole plasma. Below \(-25 \) V, \( E_F \) is far from the Dirac point. From the correlation between \( E_F \) and the total carrier density \( N \), \( E_F = h\nu_F(\pi N)^{1/2} \), it is expected that the carrier density increases in a nonlinear manner with the gate bias, \( V_g \sim \sqrt{N} \). It is clearly seen in Figure 2b that the sheet conductivity of graphene grows as a function of \( \sqrt{N} \) with the gate bias, a distinct characteristic of the two-dimensional Dirac fermion of graphene unlike conventional semiconductors. The shaded area in Figure 2b shows fittings of the Drude model with a scattering time of 32 fs (lower boundary) and 39 fs (upper boundary); the line is a guide to the eye. Note that the total carrier density of the graphene channel \( N \) is given by \( N = (n_0^2 + n_{\text{gate}}^2)^{1/2} \), where \( n_0 \) is the impurity density and \( n_{\text{gate}} \) is the carrier density induced by the gate voltage. According to the gate capacitance \( C_p \), \( n_{\text{gate}} \) is given by \( n_{\text{gate}} = C_p(V_{\text{cap}} - V_g)/\epsilon \), where \( V_{\text{cap}} \) is the voltage at

![Figure 2](image-url)
Table 1. Electrical Properties Obtained from THz-TDS and Hall Measurements

<table>
<thead>
<tr>
<th>Gate bias [V]</th>
<th>Scattering time [fs]</th>
<th>Sheet resistivity [Ω]</th>
<th>Mobility [cm²/(V s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene no. 1</td>
<td>0</td>
<td>24.3</td>
<td>1235</td>
</tr>
<tr>
<td>graphene no. 2</td>
<td>0</td>
<td>48.8</td>
<td>607</td>
</tr>
<tr>
<td>doped graphene no. 1</td>
<td>-45</td>
<td>30.9</td>
<td>985</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>THz-TDS measurement</th>
<th>Hall measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheet resistivity [Ω]</td>
<td>Mobility [cm²/(V s)]</td>
</tr>
<tr>
<td>graphene no. 1</td>
<td>1039</td>
</tr>
<tr>
<td>graphene no. 2</td>
<td>2062</td>
</tr>
<tr>
<td>doped graphene no. 1</td>
<td>1303</td>
</tr>
</tbody>
</table>

indicating a large change in $E_F$ resulting from the donation of electrons to the graphene. At the CNP of each graphene, the average sheet conductivities and the frequency-dependent sheet conductivities of the doped and undoped graphene are similar, as shown in Figure 3a,b. Furthermore, the extracted Drude scattering times for doped and undoped graphene are in a similar range, 30 fs, across the gate-voltage range, as shown in Figure 3c. The above results lead us to conclude that the electrodynamics of graphene is affected only slightly by chemical modification. This is probably due to the weak binding between graphene and viologen; it is van der Waals interaction rather than the covalent binding of interstitial or substitutional doping. More important, chemical doping could provide a way to control the carrier density without perturbing the carrier dynamics, potentially benefiting graphene-based high-speed electronics.

We also compare our THz-TDS measurements to Hall measurements. Hall measurements provide direct current (dc) conductivity, which is different from THz dynamic conductivity. We can qualitatively compare the dc and optical conductivity using the following relations: $\sigma(\omega) = \sigma_{dc}/(\omega^2\gamma^2+1)$, $\rho^{-1} = \sigma_{dc}$, and $\mu = (e\rho)^{-1}$. To measure the electrical properties at a given carrier density, the gate bias was fixed at -45 V for doped graphene to match the similar carrier density for undoped graphene (see Figure 3a). Table 1 summarizes the extracted values from the THz-TDS and Hall measurements. For the undoped graphenes, the mobility and sheet resistivity at the CNP from the THz-TDS measurements are comparable to those of the Hall measurements. The mobility and sheet resistivity from the THz measurements are 40% larger than those from the Hall measurements. This discrepancy is attributed to environmental effects. The THz measurements were taken inside a chamber with a humidity level below 3%, whereas the Hall measurements were taken in air. The residual impurity charges can easily be influenced by the ambient conditions. Nevertheless, the electrical properties characterized by the above approaches are commensurate. What is more important is the electrical properties of the doped graphene. The scattering time, sheet resistivity, and mobility are not significantly influenced by the chemical doping. This indicates that chemical doping is a promising method for building n-MOS FET without losing carrier mobility.

To conclude, we have performed THz spectroscopic measurements on CVD-grown graphene FETs. We have explored the gate-controlled electrodynamics of the two-dimensional Dirac fermion. The measured optical conductivity did not depend on the gate voltage for low carrier densities. However, for high carrier densities, we observed $\sigma(\omega) \sim \sqrt{N}$. The interaction of extrinsic doping with graphene is small and weak, suggesting that chemical modification is an efficient method for controlling the equilibrium Fermi level without sacrificing the electrodynamics of graphene.

**REFERENCES**


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**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information contains a variety of characterizations for CVD-grown monolayer graphene. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author
*E-mail: (J.-H.S.) joohiuk@uos.ac.kr; (Y.H.L.) leeyoung@skku.edu.

Author Contributions
*These authors contributed equally to this work.

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