Invited Paper

Effect of high-optical excitation on the ultrafast electron dynamics in stacked-monolayer graphene samples

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ABSTRACT

We report on transient absorption experiments performed at high optical excitation fluences and used to study the ultrafast dynamics in graphene. We employed a degenerated scheme of pump and probe at 800 nm (1.55 eV). The time resolution of our measurements was limited by the pulse duration ~ 100 fs. The samples were prepared by chemical vapor deposition (CVD) as single-layers on silica and, then staked layer-by-layer in order to make a stack of up to 5 graphene monolayers. We observed saturable absorption (SA) and fluence-dependent relaxation times. We see that the ultrafast carrier dynamics is composed by two decay mechanisms, one with response time of about 200 fs and a slower process of about 1 ps. The fast decay, due to both carrier-carrier and carrier-optical phonon scattering, becomes slower when the density of excited carrier was increased. We implemented a theoretical model and found that both the optical phonon rate emission and the optical phonon lifetime are affect by the pump fluence.

Keywords: ultrafast spectroscopy, graphene, high-fluence excitation, saturation absorption

1. INTRODUCTION

Graphene, a 2D material built from highly-packed carbon atoms, has recently emerged as a promising crystal for new optoelectronics applications[1-5]. Owing to its linear energy dispersion, graphene can absorb light over a large band of optical frequencies ranging from THz to visible spectrum. Taking into account its thickness (~ 0.345 nm), graphene absorption is very high, ~ 2.3 %[6]. Graphene also shows ultrafast absorption saturation due to Pauli blocking and rapid carrier relaxation that occurs as a result from the strong electron-phonon coupling[7,8]. This fast electron dynamics has allowed the demonstration of the use of graphene as saturable absorber for the designing of photonic devices such as ultrafast mode-locked lasers and optical modulators[7,8]. In order to improve the performance of these devices it is important to have a high modulation depth and simultaneously to conserve the ultrafast electron dynamics. One straightforward way to reach that goal is to increase the number of graphene layers. Nevertheless, this may be detrimental in samples with highly-oriented stacking graphene samples as the two-photon absorption (TPA) becomes significantly large and then, the modulation depth could be decreased[9,10]. An alternative to overcome this problem is to use stacked graphene-monolayer samples wherein the random position of carbon atoms between adjacent layer turns its TPA much smaller than, e.g., in Bernal-stacked bilayer graphene (> 100 times smaller).

Extensive experimental and theoretical studies have been done to understand the electron dynamics in graphene excited by optical pulses[11-18]. From there, it has been possible to identify the main physical mechanisms responsible for the cooling of the excited electron: immediately after the optical excitation, a non-equilibrium carrier population is put into the conduction band with the same spectral distribution of the excitation pulse. Then, within less than 50 fs, electron population reaches an internal thermal equilibrium and forms a hot Fermi-Dirac distribution (FDD) at high temperature. This hot FDD initially cools down within the next ~200 fs by emission of optical phonons (optical phonon energy ~200 meV) and thus, a subsystem of coupled electron-optical phonon is formed. Finally, that subsystem reaches thermal equilibrium with the lattice through coupling to acoustic phonons on a time scale of the order of picoseconds. It is important to mention that much of this studies have been performed at low pump fluence, much lower than those

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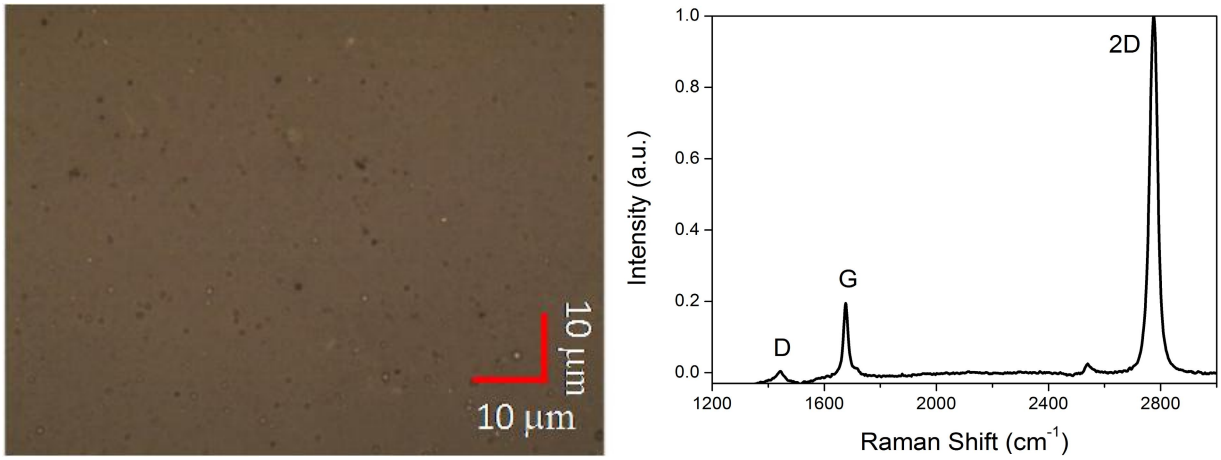
required to reach the saturation regime. Therefore, there is no clear understanding about the electronic dynamics at high enough optical excitation for which absorption saturation is reached. In this work, we explore the ultrafast electron relaxation of a 5-layer-stacked graphene sample when it is optically excited by an intense pulse in order to achieve the absorption saturation regime.

2. SAMPLE PREPARATION AND BASIC CHARACTERIZATION

Graphene samples were fabricated by chemical vapor deposition (CVD) method and transferred layer-by-layer onto glass substrates (thickness ~140 μm). The stacking process is made by fixing only one monolayer graphene at a time and thus, repeating the processes to obtain the number of desired graphene layers. It is important to note that the nature of the process is such that the relative orientation between adjacent layers is random. It is expected the interlayer interaction to be negligible in those samples, ensuring that the results found in this work for samples of stacked graphene can be interpreted as being equivalent of single graphene monolayer[19]. For this study, we have employed a sample with five stacked graphene monolayer aiming to improve the signal-to-noise ratio in our measurements. In order to characterize our samples, we measured their Raman spectra. For that we have used a Micro Raman system (Xplora - Horiba), which utilizes a laser at 532 nm as optical excitation and covers a spectral range from 100 to 3500 cm^{-1}. The main results are presented in Figure 1. From the ratio $I_G/I_{2D} < 0.5$, we can conclude that the stacked-graphene sample has the same Raman spectrum as a graphene monolayer sample.



(a) (b)

Figure 1. (a) Optical microscopy image (taken by using a 10X objective lens). The black points come from imperfections of the microscope lens. (b) Raman spectrum from the region observed in (a). The ratio $I_G/I_{2D} < 0.5$, which indicates the presence of monolayer graphene.

3. EXPERIMENTAL SETUP AND METHODS

In this work, we measured the differential transmittance of a probe pulse with (T) and without (T_0) the presence of an intense excitation pulse (pump pulse) as function of their relative delay time. The differential transmittance is simply the normalized change on the transmittance of the probe pulse defined as $\Delta T/T_0 = (T-T_0)/T_0$. The transmittance is related to the optical conductivity, $\sigma(\omega)$, by[12]:

$$T(\omega) = \frac{1}{\left(1+\sigma(\omega)\sqrt{\mu_0/\varepsilon_0}\left(1+n_{glass}\right)\right)^2}, \quad (1)$$

where ω is the optical frequency of the probe pulse, n_{glass} the refractive index of glass substrate and $\sigma(\omega)$ is given by:

$$\sigma(\omega) = -\frac{e^2}{4\hbar}\left[f_e(\hbar\omega/2) - f_h(-\hbar\omega/2) \right]. \quad (2)$$

Here, $f_{e,h}(\pm\hbar\omega/2)$ refers to the Fermi-Dirac probability of occupation in the electron energy level at $\hbar\omega/2$ in either conduction or valence band. Therefore, it is clear that the transmittance can change because of variations of carrier populations created by the optical pump excitation. That means that the recovery of the equilibrium can be tracked by measuring the changes ΔT as a function of delay time between the pump and probe pulses.

The experimental setup used in this work is shown in Figure 2. Femtosecond pulses were generated in a Ti:sapphire amplifier centered at 800 nm and with a repetition rate of 1 kHz. The pulse duration (FWHM) was estimated to be about 100 fs. A small fraction of the laser was used as the probe beam. The pump (probe) beam was focused onto the sample creating a spot size of 80 μm (40 μm) in diameter. The probe pulse was detected by a Si amplified photodetector. The pump (probe) was modulated at 500 Hz (333 Hz) using a chopper and the signal measured with a phase-sensitive lock-in amplifier.

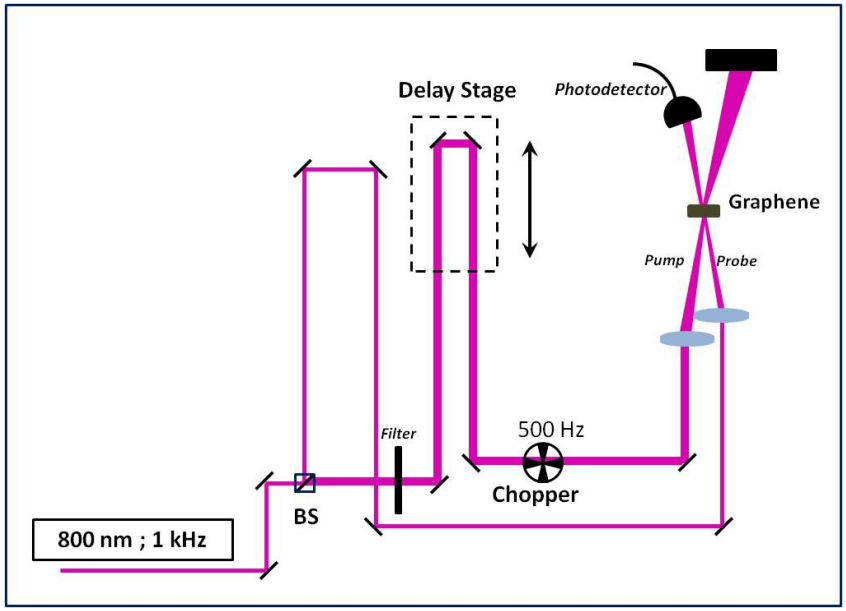


Figure 2. Pump-and-probe experimental setup utilized for transient absorption measurements in graphene samples.

4. RESULTS AND DISCUSSION

First of all, we determined the temporal resolution of our experiment through the autocorrelation of pump and probe pulses. That was obtained from the second harmonic generation (SHG) produced when the two pulses interact in a BBO (Beta Barium Borate) nonlinear optical crystal. The SHG signal was measured as a function of relative time delay between the pulses. Figure 3 shows the summarized results. From that, we can see clearly that the pump-and-probe signal observed in our experiments is not limited by the experimental time resolution.

In order to make sure we are exploring the graphene nonlinear absorption regime in our experiments, initially we have measured the differential transmittance peak as a function of the density of excited carriers (DOC), which is calculated based on the photon flux and the graphene absorption. It can be seen in Figure 4(a) that the ΔT_{MAX} increases linearly for DOC less than $2x10^{14}$ cm^{-2} and then the saturation regime is reached. In this way, we are able to study the dynamics in the linear and nonlinear regime. We measured the temporal evolution of ΔT for several DOC. Figure 4(b) shows the main results for the transient differential transmittance. According to previous reported results, we see that the electron relaxation dynamics is governed by two characteristic decay time: one fast (τ_1), associated to emission of optical phonon

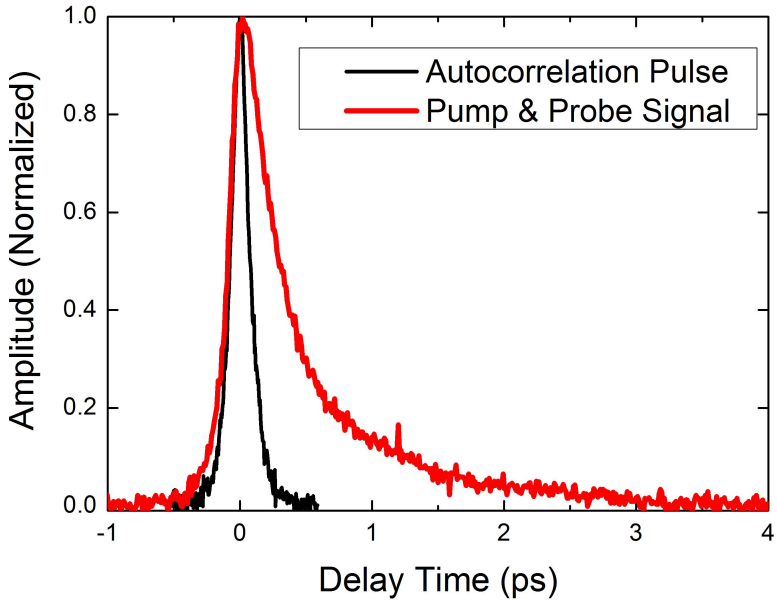


Figure 3. Autocorrelation and transient absorption signal generated from glass substrate and glass+graphene sample. The time resolution is ~100 fs and the contribution from the substrate can considered negligible.

by the excited electrons and another slower (τ_2) caused by the cooling of the coupled electron-optical phonon system through the emission of acoustic phonons. In order to explore the possible dependence of those decay times with the DOC, we fitted the experimental curves using a bi-exponential function and summarized the results in Figure 5. The nonlinear fitting shows that the fast decay time starts from 130 fs (nearly limited by our resolution) and increases up to a constant value of ~ 190 fs (see Figure 5.(a)). Additionally, we found that the slow decay constant barely changed over the range of DOC explored in this experiment, maintain around 0.8 ± 0.1 ps. The contribution of the slow component to the global relaxation dynamics increases with the DOC as it is revealed by the ratio between the amplitudes (A_2/A_1) vs DOC in the Figure 5(b).

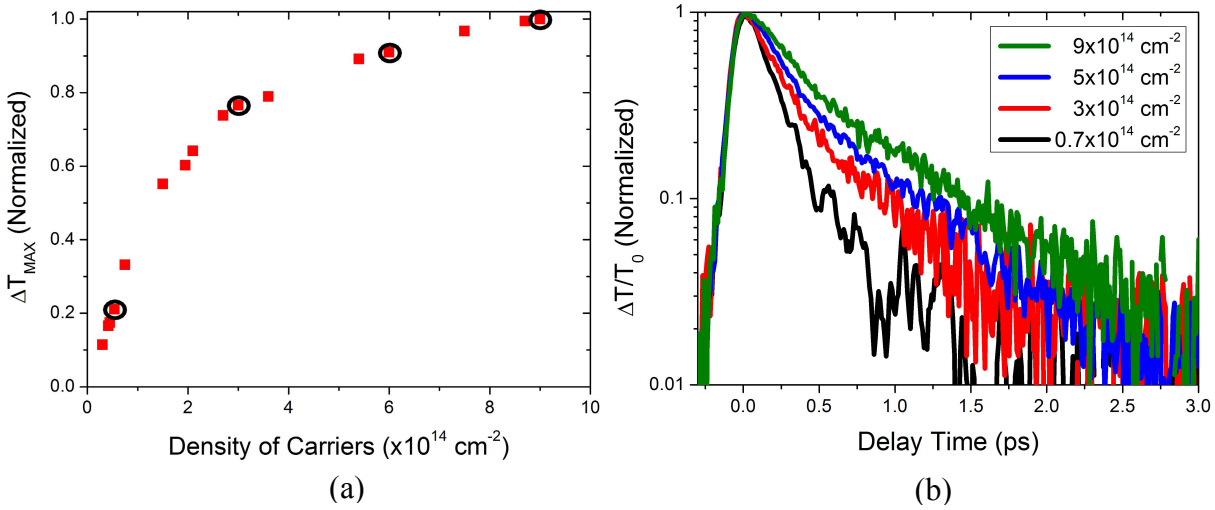


Figure 4. Experimental data for (a) the maximum differential transmittance as a function of density of excited carriers by the pump pulse and, (b) the transient transmittance as a function of the delay time. Each graph in (b) corresponds to the DOC marked with the black-circles in (a).

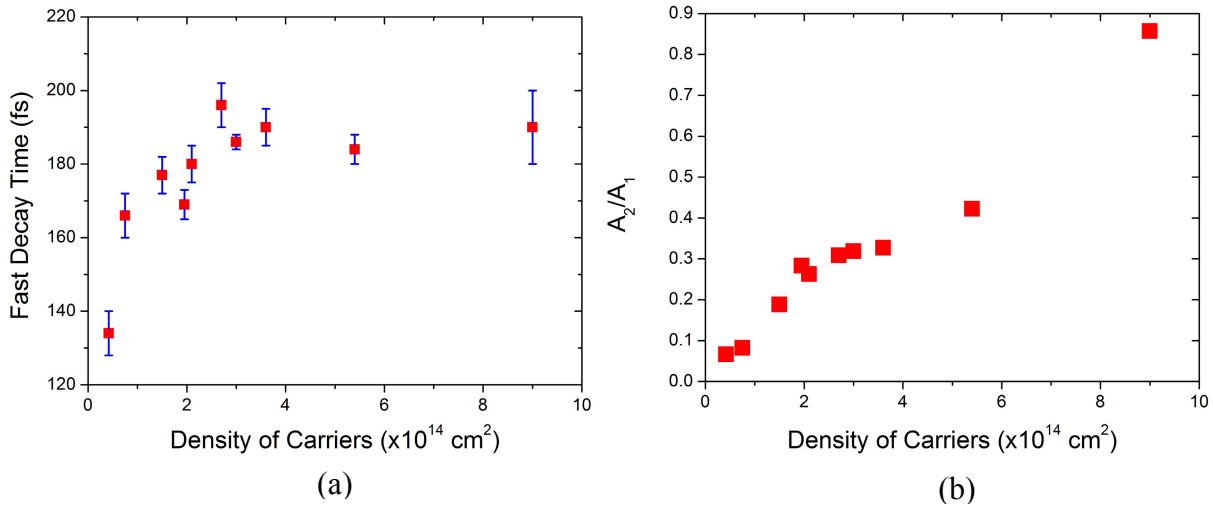


Figure 5. (a) Fast decay time component and (b) the ratio A_2/A_1 as a function of density of excited carriers. Both results were obtained after of fitting the experimental data using a bi-exponential function.

In order to shine some light on the physical mechanisms responsible for those results, we must examine in detail the well-established electron-relaxation processes in graphene. Before the arrival of the pump pulse, carriers (electrons) and the graphene lattice are in thermal equilibrium at room temperature. Then, during the optical pumping, electrons are excited from the valence to the conduction band and reach a quasi-equilibrium temperature to form a hot Fermi-Dirac distribution. After the pump excitation ends, the hot carriers cool down by emitting optical phonon ($\hbar\omega_{op}$ ~200 meV per event). Finally, when a large part of the carrier distribution is below $\hbar\omega_{op}$, the coupled system of carriers-and-optical phonon cools down even further through the generation of acoustic phonon. At high density of excited carriers a large number of optical phonon is also generated. That creates a bottleneck for the carrier cooling and the slow decay time increases with the DOC[20,21]. Nevertheless, neither we observe a significant increase of the slow decay time nor the growing of τ_1 cannot be attributed to that mechanism because their effects happen on a longer time scale (~ 1 ps).

For grasping a deeper understanding of that particular feature, we used the theoretical model proposed by Wang[13] which assumes an initial hot-carriers distribution at high temperature equilibrium (T_e) coupled to a bath of optical phonons. Those phonons start from room temperature distribution (300 K) and are assumed to go back to thermal equilibrium into a characteristic time, τ_{op}. The set of coupled differential equations governing the relaxation electron dynamics is[13],

$$\frac{dT_e}{dt} = \frac{R_\Gamma \hbar\omega_\Gamma + R_K \hbar\omega_K}{C_e}, \tag{3}$$

$$\frac{dn_\Gamma}{dt} = \frac{R_\Gamma}{M_\Gamma} - \frac{n_\Gamma - n_{\Gamma,0}}{\tau_{op}}, \tag{4}$$

$$\frac{dn_K}{dt} = \frac{R_K}{M_K} - \frac{n_K - n_{K,0}}{\tau_{op}}, \tag{5}$$

where $\hbar\omega_\Gamma$ ~ 196 meV ($\hbar\omega_K$ ~ 161 meV) corresponds to the energy of the Γ-mode optical mode (K-), C_e is the electron heat capacity[22], n_Γ (n_K) is the optical phonon occupation and $n_{\Gamma,0}$ ($n_{K,0}$) is its value at room temperature[13]. M_Γ (M_K) is the number of optical phonon modes per unit of area involved in the relaxation electron process. We calculate its value and found it equals 2.21x10^{13} cm^{-2} (2.26x10^{13} cm^{-2}). Finally, R_Γ (R_K) is the net optical phonon emission rate in the Γ-mode (K-mode) and it is given by[13],

$$R_\Gamma = 9\frac{(dt/db)^2}{\pi\rho\omega_\Gamma\hbar^4 v_F{}^4}\int_{\hbar\omega_\Gamma}^{\infty} dEE\left(E-\hbar\omega_\Gamma\right)$$
$$\times\left\{f_e\left[1-f_e\left(E-\hbar\omega_\Gamma\right)\right]\left(n_\Gamma+1\right)\right. \quad (6)$$
$$\left.-f_e\left(E-\hbar\omega_\Gamma\right)\left[1-f_e\left(E\right)\right]n_\Gamma\right\}.$$

In this expression, dt/db has a value of 45 eV/nm, v_F is the Fermi velocity of electrons in graphene, 10^6 m/s, and ρ is the density of graphene. Equivalent expression for R_K is found when ω_Γ is substituted by ω_K. It is important to note that R_Γ dependents on electron temperature through f_e. By using of equations from (1) to (6), we fitted the experimental results in Figure 4.(b). The fitting parameters are the initial electron temperature, $T_{e,0}$, and the lifetime of the optical phonons, τ_{op}. The results are shown in the Figure 6. The ultrafast response of graphene was convoluted with a Gaussian pulse (FWHM pulse duration ~ 100 fs). We found that both the carrier and optical phonon temperatures increases slightly as the pump fluence rises. But the increasing of carrier temperature was not as large as it was the increasing of optical lifetime. The fit results show that the optical phonon lifetime starts from 0.2 ps and goes up to 0.8 ps. Therefore, those results suggest that both optical phonon rate emission and unknown saturation of relaxation of optical phonons are responsible for the increasing of relaxation decays times of carriers in our samples of stacked graphene monolayer. Nevertheless, when we calculated the density of excited carrier using the values for the maximum carrier temperature given by the theoretical model we discovered that they are very low (~10^{12} cm^{-2}) compared with those experimentally estimated (~10^{14} cm^{-2}). Accordingly, we suggest a revision of the two-temperature model at the saturation regime of optically excited graphene samples.

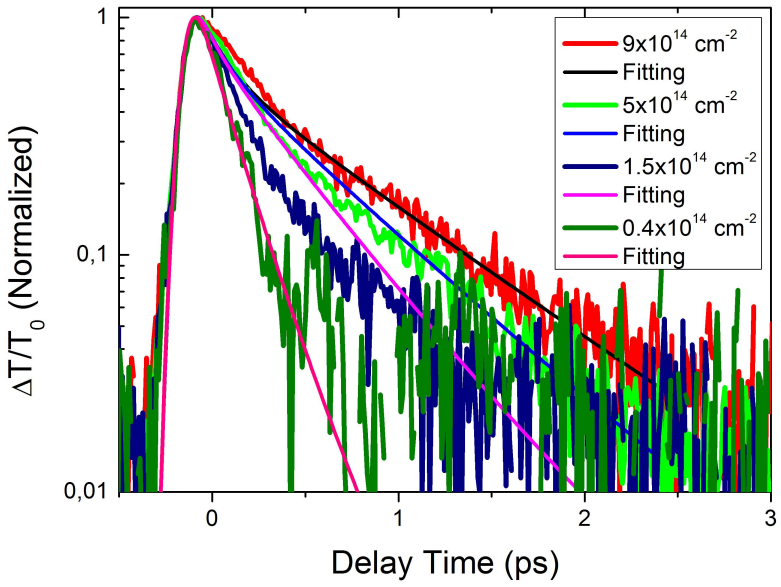


Figure 6. Experimental data fitted using theoretical model. Note that it is necessary to change the initial electron temperature but not the slow decay time associated to optical phonon relaxation.

5. CONCLUSIONS

We study the relaxation electron dynamics in 5-layer stacked graphene sample. We focus on the saturation regime which is achieved when the sample is excited with a high-fluence pulsed laser. We found that the ultrafast electron dynamics is governed by two physical mechanisms characterized by two decay times. Initially, we fitted our experimental results using a bi-exponential decay function and we found that the slower decay time barely changes with the optical fluence, but the faster one increases notoriously as pump fluence rise. However, when experimental data are analyzed using a

two-temperature model, we discovered that both the fast decay time (associated to optical phonon emission rate) and the slower decay time (related to optical phonon lifetime) increased as a function of pump fluence. Therefore, both carrier relaxation mechanisms are affected at high pump fluences. We found that the carrier temperatures given by the theoretical model are not compatible with those calculated from the experimentally estimated values for the density of excited carriers. Then, it is important to take account this issue in future studies treating the ultrafast dynamics of graphene at high optical excitations.

6. ACKNOWLEDGMENTS

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