# Ultrafast carrier kinetics in exfoliated graphene and thin graphite films

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**Abstract:** Time-resolved transmissivity and reflectivity of exfoliated graphene and thin graphite films on a 295 K SiO<sub>2</sub>/Si substrate are measured at 1300 nm following excitation by 150 fs, 800 nm pump pulses. From the extracted transient optical conductivity we identify a fast recovery time constant which increases from ~200 to 300 fs and a longer one which increases from 2.5 to 5 ps as the number of atomic layers increases from 1 to ~260. We attribute the temporal recovery to carrier cooling and recombination with the layer dependence related to substrate coupling. Results are compared with related measurements for epitaxial, multilayer graphene.

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**OCIS codes:** (320.7130) Ultrafast processes in condensed matter, including semiconductors; (160.4236) Nanomaterials.

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### 1. Introduction

Graphene is a single two-dimensional atomic layer of carbon atoms arranged in a hexagonal lattice [1,2]. Electronically, as an isolated film, it is a zero band gap semiconductor with a linear dispersion relation in the vicinity of the K and K' points of the Brillouin zone. Electrons in the vicinity of the band gap behave as zero mass Dirac fermions, unlike electrons associated with parabolic bands in, e.g., bulk semiconductors. Novel quantum and transport properties [3,4] in graphene have made this material the focus of fundamental physics [5,6] as well as a possible platform for new types of nanoelectronic devices. It has been shown theoretically [7] that as one forms multilayer structures based on (hexagonal Bernal) ABAB-stacking, the electronic structure and many properties of graphene evolve to those of graphite by approximately 10 layers. Knowledge of ultrafast, hot carrier kinetics and how they evolve with number of layers is essential for many applications. We have therefore examined how these kinetics change by studying exfoliated thin films with 1 layer (graphene), 2 layers, etc., up to 260 layers by probing the time-resolved reflectivity and transmissivity.

To date, the most popular methods for producing graphene are epitaxial growth and exfoliation. In the former case, the vacuum graphitization of SiC to high temperatures results in  $\sim$ 5-40 layers of graphene [8-10], whereby the first layer next to the SiC is often doped (metallic). Despite the multilayer nature, evidence suggests that this structure has many of the characteristics of a single graphene layer [11-15]. This has been attributed to a different stacking structure [15] compared to hexagonal Bernal graphite, resulting in an effective

decoupling of adjacent layers. However, it is difficult to control and measure the number of graphene layers and the structures normally possess a non-negligible degree of disorder and/or defects. In the exfoliation fabrication method, different layer thicknesses of graphene/graphite are obtained by micromechanically cleaving bulk graphite [2] and attaching the layers to, e.g. quartz or oxidized silicon substrates. Uniform samples with diameters of tens of microns are produced, large enough for many transport and optical experiments. The use of the SiO<sub>2</sub>/Si substrate has been used by many groups, since for an oxide thickness of 300 nm, it is possible to determine the number of carbon layers, including observing graphene itself, through visible optical interference effects [16,17], Raman spectroscopy [18] or atomic force microscopy, with each technique having merit depending on the number of layers. Relative to epitaxial growth, the exfoliation technique provides relatively defect-free graphene samples, as well as thin films of hexagonal Bernal graphite, i.e. the capability of generating many samples with a wide range of thicknesses. While the epitaxial technique may offer a better long-term platform for future devices, exfoliation allows one to determine how properties such as the ultrafast carrier kinetics examined here evolve in passing from graphene, the true one layer structure, to multilayer graphite. By mounting the samples on a SiO<sub>2</sub>/Si substrate and using optical visibility, Raman spectroscopy and atomic force microscopy, we can clearly identify the sample layer thicknesses. Both reflectivity and transmissivity are considered, allowing us to extract both the real and imaginary parts of the optical conductivity change.

Recently there have been reports on the ultrafast carrier dynamics of epitaxial graphene. Dawlaty et al. [19] have studied ultrafast optical transmissivity of a few samples with between 6 and 37 layers using 85 fs, 780 nm pump and probe beams. From the nonexponential time dependence of the transmissivity recovery, they assign a fast time constant of ~70-120 fs to carrier thermalization, and a slower time constant of  $\sim 0.4$ -1.2 ps to carrier cooling. The dependence of the latter time constant on sample was attributed to the degree of crystalline order. More recently, D. Sun et al. [20] have reported time-resolved transmissivity on an epitaxial sample. The first layer was doped with an electron concentration of  $9 \times 10^{12}$  cm<sup>-2</sup>, resulting in an electron Fermi level of  $\sim 350$  meV. The remaining estimated 15-20 layers were neutral. Time-resolved transmissivity was recorded at different temperatures with 150 fs probe pulses between 1.57 and 2.4 µm following a 800 nm, 150 fs pump beam. The timeresolved transmissivity is therefore a measure of the response of both doped and undoped layers. As with the work of Dawlaty et al., a non-exponential decay of the transmissivity was observed but this was postulated to be a stretched exponential decay. Possible sources for the non-exponential behavior were suggested to be hot-phonons, sample disorder and densitydependent carrier scattering.

## 2. Experimental

Our graphene samples were fabricated from natural flake graphite by micromechanical cleaving with transparent tape followed by application onto a 500  $\mu$ m thick Si substrate with a 300 nm SiO<sub>2</sub> surface layer. Samples used in the experiments had between 1 and 260 layers and had uniform thickness over a circular area of at least 15  $\mu$ m in diameter. Samples with up to seven layers can be distinguished using an optical microscope, due to the optical interference effect. Samples between one and three layers were confirmed using Raman Spectroscopy. For the thicker samples, atomic force microscopy was used to determine the number of layers with an accuracy of ±10%. Raman spectra of the thin samples showed no defect-induced D lines [21]. The Si wafer was slightly n-doped, however the free electron concentration of ~1x10<sup>18</sup> cm<sup>-3</sup> was sufficiently low to allow for significant transmission at our probe wavelength.

For the time-resolved optical experiment, an 80 MHz Ti:sapphire oscillator provides 1.0 nJ 150 fs pump pulses at 800 nm, while simultaneously pumping an 80 MHz OPO system delivering 2.5 pJ 150 fs probe pulses at 1300 nm. The probe wavelength was chosen to be below the indirect Si band gap so that only free carrier absorption can occur. The probed electron and hole-coupled states are within the linear regime of the electron dispersion relation. After the probe's optical delay line, the collinearly polarized pump and probe beams

were focused through a 40X (numerical aperture = 0.65) objective onto the samples that were held at room temperature (295K). Samples were positioned to be at the focal plane of the probe beam and not the pump beam, which provided a pump spot diameter (~20 µm FWHM) greater than the probe spot diameter (~3 µm FWHM). This assured the probe-sampled area experienced uniform excitation. For an optical absorption of ~2%/layer in graphene and an incident pump photon flux of  $< 10^{15}$  cm<sup>-2</sup>, we estimate a peak carrier density per layer  $< 10^{13}$  cm<sup>-2</sup>. In the case of silicon, for which the absorption depth of the pump beam is ~12  $\mu$ m, the estimated induced peak carrier density is ~10<sup>17</sup> cm<sup>-3</sup>. If only optically generated electrons and holes are produced, the maximum carrier temperature, following thermalization, could be several thousand Kelvin. However, the presence of thermally activated carriers or (unintentional) doping will reduce this temperature. The pump intensity was kept well below the damage threshold of graphene, which was confirmed by the lack of both visual damage and defect-induced D lines in the Raman spectra before and after the pump-probe experiments. Samples were imaged in a confocal arrangement with a CCD camera. Transmitted and reflected probe beams were measured with biased Ge photodiodes and a lock-in amplifier. It was verified that all reflectivity and transmissivity signals were linear in probe intensities up to the maximum intensity reported here. At the probe wavelength the unexcited complex refractive indices of Si, SiO<sub>2</sub> and graphite are  $3.543+1.5\times10^{-4}$  i, 1.45, and 3.27+2.54i respectively.

### 3. Results

For each of the graphene/graphite samples, as well as the bare SiO<sub>2</sub>/Si region immediately surrounding it, the time-resolved differential change in reflectivity ( $\Delta R/R$ ) and transmissivity ( $\Delta T/T$ ) were measured for up to 35 ps of probe delay. Samples with 0 (bare SiO<sub>2</sub>/Si), 1, 2, ... 260 layers were measured; a subset of these measurement for the time delay interval -2 to 15 ps are shown in Fig. 1.



Fig. 1. Time-dependent differential reflectivity  $\Delta R/R$  and transmissivity  $\Delta T/T$  of graphene/ graphite samples with number of carbon layers indicated.

Received 15 Dec 2008; revised 30 Jan 2009; accepted 3 Feb 2009; published 5 Feb 2009
16 February 2009 / Vol. 17, No. 4 / OPTICS EXPRESS 2329

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The SiO<sub>2</sub>/Si time-resolved reflectivity appears to be similar to that of Sabbah and Riffe [22], although for their probe wavelength of 800 nm, the measured transient optical properties are dominated by interband absorption whereas ours are dominated by free carrier absorption. The nonzero initial value (*i.e.*, before a particular pump pulse arrives) of the reflectivity and transmissivity occurs because of some steady-state carrier accumulation effects in the silicon since the recombination time is longer than the inter-pulse separation time of  $\sim 12.5$  ns. The results from bulk graphite are also in agreement with the results of Seibert et al. [23] after correcting for the difference in probe wavelengths. Their data was obtained with visible and near infrared probe wavelengths. As the wavelength increases, the optically probed electron and hole states are closer to the band edge and Fermi level, and the apparent relaxation time increases [23]. From the data in Fig. 1, one can observe that as the number of graphene layers increases, the signals becomes increasingly different from that of the bare substrate, with the Si exhibiting less and less of an effect due to increasing absorption from the carbon layers. For > -25 layers we observe the typical behavior of bulk graphite [23]. Note that at the extremes of layer number, *i.e.* for the bare SiO<sub>2</sub>/Si and bulk graphite, the signals are very different, with Si showing a very long recombination time, while the graphite change recovers within 15 ps.

To extract the time-dependent optical properties of the carbon layers we model the entire multilayer system with a transfer matrix method. For samples with < ~100 layers, the fact that both the Si and the carbon layers are contributing to the change in reflectivity and transmissivity must be taken into account; the oxide layer is assumed to be inert. In particular the optical response of the Si needs to be isolated from the effect of the graphene/graphite. To do this, the change in the Si complex optical conductivity is first determined from the  $\Delta R/R$  and  $\Delta T/T$  experimental data for the bare SiO<sub>2</sub>/Si substrate. This information can then be used in our multilayer model to compute the change in the graphene/graphite optical conductivity from the  $\Delta R/R$  and  $\Delta T/T$  experimental data on our samples. The fact that silicon's optical response includes a decay time much greater than that of graphite aids in determining the magnitude of the effect from silicon in our multilayer sample. In essence, for times > 20 ps we can assume the graphene/graphite material properties have returned to their quiescent values and the silicon is the only material contributing to the nonzero differential reflectivity and transmissivity. This allows us to scale the material changes accordingly to get the most accurate view of the effects occurring only in graphene/graphite.

The transfer matrix method [24] is used to numerically compute the relative changes in the real and imaginary parts of the optical conductivity,  $\Delta \sigma_R / \sigma_R$  and  $\Delta \sigma_I / \sigma_I$  respectively, from  $\Delta R/R$  and  $\Delta T/T$ . Each of the individual carbon layers can be represented by a transfer matrix, with  $\Delta \sigma_R$  and  $\Delta \sigma_I$  decreasing into the sample from the illuminated face according to the graphite pump absorption. We take each layer's quiescent optical properties as those of bulk graphite with a thickness of 0.335 nm; such an assumption for visible and near visible light has worked well in determining the sample thickness [15,16]. When the SiO<sub>2</sub> and Si layers are included, the total reflection and transmission amplitude coefficients can be computed and used to obtain  $\Delta R/R$  and  $\Delta T/T$ . At each time delay the  $\Delta \sigma_R / \sigma_R$  and  $\Delta \sigma_I / \sigma_I$  values are chosen to obtain the  $\Delta R/R$  and  $\Delta T/T$  values observed.

In this way, we use the time-resolved reflectivity and transmissivity data to deduce the time dependence of  $\sigma_R$  and  $\sigma_I$ . This dependence is shown in Fig. 2 for a select set of samples. The particular values of differential conductivity plotted are those for the top layer in our multilayer samples. The changes will, of course, be smaller for layers closer to the substrate where the pump intensity will be lower. For all our samples, the  $\Delta \sigma_R / \sigma_R$  show a similar type of behavior, *i.e.*, a rapid decrease during the pump pulse followed by a non-exponential recovery. However, the  $\Delta \sigma_I / \sigma_I$  data sets show different behavior as the number of layers increases. We observe that for 1-3 layers, except for some behaviour around the pulse overlap time,  $\Delta \sigma_I / \sigma_I$  shows a magnitude that is clearly non-zero and a non-exponential

time dependence similar to that of  $\Delta \sigma_R / \sigma_R$ . For the thickest samples, the behavior of both real and imaginary parts of the optical conductivity are similar to that observed previously for graphite [23].

For the single layer material (graphene) the overall behavior of  $\Delta \sigma_R / \sigma_R$ , *i.e.*, the decrease and non-exponential recovery on a time scale of several ps, is similar to that observed by other groups [18,19] carrying out related experiments for epitaxially grown graphene. In our case these characteristics persist, and indeed, evolve only slightly as the sample thickness increases. The Cornell group [18] chose to model the non-exponential recovery as a double exponential while the Michigan/Georgia group modeled the non-exponential recovery as a stretched exponential [19]. We can fit both types of behavior to all our data, although there is a noticeable discrepancy between the data and the stretched exponential fit, especially for samples giving high signal/noise ratios. The fact that our extracted characteristic time constants differ by approximately a factor of 10 helps in obtaining these two parameters. For this reason and since other groups have suggested sources of double exponential behavior in the optical response due to, *e.g.*, two types of carrier cooling mechanisms [25] or combinations of cooling and recombination [26] we proceed with fitting our data to a double exponential function convolved with the Gaussian pump and probe pulse profiles.



Fig. 2. Extracted time-resolved  $\Delta \sigma_R / \sigma_R$  and  $\Delta \sigma_I / \sigma_I$  for the top layer of graphene/ graphite samples with number of carbon layers indicated.

The two time constants extracted from the  $\Delta \sigma_R / \sigma_R$  data are shown for samples with up to 260 layers in Fig. 3. Note that the error bars not only reflect experimental uncertainty due to measurements on a particular sample, but also variation in different samples with the same number of layers. The fast time constant increases, at best only slightly, from ~200 fs to ~300 fs over a few layers and thereafter apparently remains constant while the slower time constant increases from 2.5 ps to 5 ps as the sample thickness increases from 1 to ~30 layers before apparently remaining constant to ~260 layers.



Fig. 3. Extracted fast and slow time constants from time-resolved  $\Delta \sigma_R / \sigma_R$  for our graphene/ graphite samples as a function of the number of layers.

# 4. Discussion

Simple expressions have been derived elsewhere for the frequency-dependent change in the inter- and intra-band optical conductivity of (2-D) graphene [27] and 3-D graphite [23] following optical excitation. In both cases, after thermalization takes place, at near infrared wavelengths  $\Delta \sigma_R$  is dominated by the change to the inter-band absorption, determined by the change in the Fermi-Dirac occupancy factor for electrons (e) and holes (h),  $f_{e(h)}$  at the optically coupled states. For a probe photon energy of  $\hbar\omega$  and a linear dispersion relation for electron and hole states, one has  $f_e(\hbar\omega/2) \propto C(T_e)N_e \exp(-\hbar\omega/2k_BT_e) = f_h(-\hbar\omega/2)$  where  $C(T_e)$  is a factor dependent on the carrier temperature,  $T_e$ , and  $N_e$  is the electron (or hole) density appropriate for 2-D or 3-D. Specifically, we expect  $\Delta \sigma_R \propto -[f_e(\hbar\omega/2) + f_h(-\hbar\omega/2)]$ . The  $\Delta \sigma_I$  is dominated by Kramers-Krönig related changes to the inter-band absorption and Drude contributions. For 2-D materials this is expected to be weak at visible and near visible wavelengths, but for 3-D materials the contribution can be non-negligible [23]. Our data is consistent with this trend, apart from transient, non-equilibrium effects during the pump pulse. For samples with substantial  $\Delta \sigma_I / \sigma_I$ , the decay characteristics are similar to those for  $\Delta \sigma_R / \sigma_R$  as discussed below and won't be considered further here.

Ignoring the strongly non-equilibrium behavior occurring during the pump pulse, we see that the reduction of  $\Delta \sigma_R / \sigma_R$  can reflect an increase in either or both of  $T_e$  or  $N_e$ ; conversely, the recovery can represent a decrease of one or both of these parameters. From previous work we know that through emission of  $\sim 200 \text{ meV}$  phonons [25] the temperature is expected to decrease on a sub-picosecond time scale and indeed our fast time constant is consistent with the  $\sim 0.3$  ps time scales reported elsewhere [25, 26]. Because of the localized nature of these high-energy phonons, the cooling dynamics associated with them is not expected to change significantly as the number of layers changes. The slight (if any) variation observed for low layer numbers is likely associated with changes in the band structure, including a band gap; this can affect the energy location of optically coupled states and states which participate in energy relaxation, as well as effective doping levels. While the Cornell group [18] has extracted a fast time constant of  $\sim 120$  fs and assigned it to the carrier thermalization as opposed to cooling processes, the use of a probe photon wavelength much shorter than ours can account for a reduced apparent cooling time. The time scales of our decay traces are consistent with that of the Georgia/Michigan group for multilayer graphene [19]; the data in both cases is obtained for > 1  $\mu$ m probe pulses. While we do not expect many-body effects

(such as those from excitons or their interactions) to contribute to our results due to the lack of spectral features at our pump and probe frequencies [28,29], we cannot eliminate them entirely based on our experiments.

The longer relation time may reflect some combination of carrier recombination and/or energy relaxation via, *e.g.*, acoustic phonon induced relaxation or reduced cooling via hot phonons [25,26]. From our optical experiments alone we cannot rule out one of these mechanisms. Acoustic phonon-induced relaxation is well known to lead to longer relaxation, since the carrier energy loss per emission event is much lower than that for optical phonons. Carrier recombination times of the order of a few ps for graphene and related materials have been reported [26]. The Cornell group has observed shorter times (~0.5-2 ps) for the slow component, but this may relate to probing with a shorter wavelength than we use or the role of defects in energy relaxation in epitaxial graphene.

The fact that the slow decay time increases gradually with number of layers hints to transport of carriers and/or thermal energy across the interface. If one makes the commonlyused assumption of no inter-layer interactions and, more importantly, no graphite-SiO<sub>2</sub> interaction, decay times should not increase after a few layers. However, the consideration of ballistic or diffusive transport could explain this trend. For example, in a simple decaydiffusion model (ballistic transport would yield even faster recovery) of carriers and/or carrier energy, using a decay time of 5 ps, a diffusion constant of 0.1 cm<sup>2</sup>/s, and a SiO<sub>2</sub> interface surface recombination constant of  $10^4$  cm/s, a similar trend is recovered. The diffusion constant is based on the known value for interlayer diffusion of heat (thermal diffusivity) [30,31]. Both the change in reflectivity and transmissivity experience decay times that increase gradually from ~2.5 ps to 5 ps in ~30 layers. While the values of these model parameters are not the point of emphasis here, the underlying mechanism associated with them does offer a possible explanation as to why this slow decay time constant increases with number of layers.

# 5. Summary

We have studied the time-resolved reflectivity and transmissivity of single and multilayer graphene/graphite mounted on a SiO<sub>2</sub>/Si substrate and extracted the time dependence of the real and imaginary parts of the optical conductivity. The kinetics indicate a non-exponential recovery of both real and imaginary parts of the optical conductivity, with fast and slow time constants that differ by an order of magnitude. In addition, we have shown how the time-dependent optical properties depend on the number of layers and suggested that this is related to transport and sample/substrate coupling. Finally, it is interesting to observe that, at least for our probe photon energies, the properties do not change substantially in proceeding from graphene to few layer samples. This is perhaps not surprising since graphite is loosely bonded layers of graphene-like planes. Some comparisons with related data in multilayer epitaxially grown graphene have been made, but one should be cautious since the two material systems are different, not only in terms of interlayer stacking but also in defect density, etc.

# Acknowledgments

We thank Sida Wang for early help in making graphene samples and Joshua Folk for advice on exfoliation. We acknowledge financial support from NSERC Canada.