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Diversity of ultrafast hot-carrier-induced dynamics and striking sub-femtosecond hot-carrier scattering times in graphene

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ABSTRACT

We study ultrafast dynamics in graphene grown by chemical vapor deposition, which presents a positive peak followed by a negative slow recovery process, and is different from the fully positive or negative dynamics reported. We discuss the diversity of ultrafast dynamics. A dynamic model of differential optical conductivity is developed to simulate ultrafast dynamics. It is found that the diversity of ultrafast dynamics originates from multiple parameter dependence. The appearance of ultrafast dynamics is mainly determined by the position of probed level with respect to static Fermi energy and/or momentum scattering time. The dynamic model is used to best fit the observed ultrafast dynamics to retrieve dynamic time constants. The thermalizing and cooling times of optical phonons are found consistent with the reported values, but a striking sub-femtosecond momentum scattering time and a sub-picosecond time of electron–hole recombination are obtained. The sub-femtosecond scattering time is much shorter than several to a few hundred femtoseconds accepted currently.

1. Introduction

The development of graphene-based high speed electronic devices requires the understanding of ultrafast carrier dynamic processes in graphene. Many researches reported on the ultrafast carrier dynamics in mono- and few-layer graphene, and revealed rich and diverse ultrafast dynamics. Dawlaty et al. first studied the ultrafast carrier dynamics in few-layer epitaxial graphene grown on 6H-SiC by thermal decomposition of SiC surface at high temperatures using near-infrared femtosecond pump–probe differential transmission spectroscopy [1], and found a pure absorption-saturated ultrafast dynamics, that is a fully positive differential transmission dynamics (DTD). Thereafter, many researches also reported on similar fully positive DTDs in few-layer graphene grown on 6H-SiC by thermal decomposition of SiC surface and grown by chemical vapor deposition (CVD) [2], in solution-processable few-layer graphene oxide and reduced graphene oxide [3], and in mono-layer graphene on SiO_2 grown by CVD [4]. Meanwhile, a fully negative

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differential reflectivity dynamics (DRD) was also reported in mono-layer graphene grown on 6H-SiC by thermal decomposition of 6H-SiC [5], which is equivalent to a fully positive DTD. In contrast, another researchers reported on fully negative DTD, that is absorption-enhanced dynamics, in mono- and a few-layer graphene grown on 6H-SiC [6], few-layer graphene grown on 6H-SiC [7], a few-layer graphene grown on 4H-SiC [8], and mono- and a few-layer exfoliated graphene on a Si substrate [9]. Similarly, a fully positive DRD was also observed in mono-layer graphene transferred on glass [10] and MgO [11] substrates grown by CVD, which was equivalent to a fully negative DTD. In addition, complex probe-wavelength-dependent evolution of DTD was also reported [12–14]. Shang et al. [12,13] and Breusing et al. [14] studied the ultrafast carrier dynamics of CVD-grown a mono- and few-layer graphene transferred on quartz substrates [12,13] and exfoliated monolayer graphene on mica substrates [14], respectively and found that DTD was fully positive as the wavelength of probe (probed level) was longer (lower). However, the dynamics was evolved into an initial positive peak followed by a slow negative recovery dynamics as the wavelength of probe (probed level) decreased (increased). Sun et al. [15] investigated the ultrafast carrier dynamics of bi-layer graphene grown on 4H-SiC by thermal desorption of Si, and found that DTD was fully positive as the wavelength of probe was slightly larger (less) than 2.35 μm (1.78 μm), whereas it became fully negative as the wavelength was located in the central part of the range of 1.78–2.35 μm. However, the dynamics was in turn evolved into an initial positive peak followed by a negative slowly decayed dynamics when the wavelength of probe was near 1.78 or 2.35 μm. Those diverse ultrafast dynamics has not been focused on and understood completely. Even some contradictory experimental results, measured on similar samples and under similar experimental conditions, have not been paid attention to yet, such as the experimental results reported in Refs. [1,8].

On the other hand, the quantitative analysis on the ultrafast dynamics was mainly based on three types of models, the biexponential decay [1,3,8–10,12], optical conductivity model in which either interband [5] or intraband [7] transition was solely taken into account and phenomenological models [2]. In principle, these models could not give accurate physical parameters unambiguously to describe real ultrafast processes occurred in graphene because they did not consider or incompletely considered the real physical processes so that the measurements of some physical parameters, such as momentum scattering time and lifetime of electron–hole recombination, have been absent or rare. The former was obtained mainly by theoretical calculation, and predicted to be in a large range of a few to a few hundreds of femtoseconds [2,7,16,17]. Meanwhile, it was also exhibited theoretically that the Fermi distribution of photoexcited carriers could be established within 100 fs [18]. Experimentally, Li et al. [5] even found the photoinjected carriers could be thermalized in 35 fs, implying a few scattering events enabling the photoinjected carriers thermalized if the scattering time of several to a few hundreds of femtoseconds is accepted [2,7,16,17]. It is evident that the experimental observation did not agree well with the theoretical prediction for the scattering time of carriers. The latter, the lifetime of electron–hole recombination, experimentally was reported rarely [6] except for theoretical calculations [19,20].

In this paper, we investigate ultrafast dynamics of photoexcited carriers in a CVD-grown monolayer graphene transferred on a quartz substrate, and find that DTD presents a first positive peak near zero-delay time, and then rapidly decays into a negative dynamics which recovers slowly back to the initial state. Such DTD is kept almost unchanged with increasing photoinjected carrier density but the amplitude of the positive and negative peaks is increased. A dynamic model of differential optical conductivity including both intra- and inter-band transitions is developed to simulate DTD for different scattering time, Fermi level, probe energy and photoinjected carrier density. The simulated results explain well the diversity of ultrafast carrier dynamics reported so far and our experimental results. Finally, the dynamic model is used best to fit our experimental results. The scattering time, lifetime of electron–hole recombination, and time constants of electron-optical phonon exchanging and optical phonon cooling are achieved. A striking sub-femtosecond hot-carrier scattering time is found, which is much less than the value of a few to a few hundred femtoseconds accepted currently.

2. Sample and experimental

The graphene sample studied here is grown on copper foil by CVD [21], and then transferred onto a thin quartz substrate as described in Ref. [22]. The sample is characterized with Renishaw in Via micro-Raman spectrometer at a laser wavelength of 514.5 nm and Perkin Elmer Lambda 900 absorption spectrometer. A Ti:sapphire self-mode-locked oscillator is used to study ultrafast carrier dynamics using transient differential transmission spectroscopy. The mode-locked laser pulse train has a repetition rate of 94 MHz, the central wavelength of 810 nm and the duration of ~80 fs. The laser pulse goes through a standard pump–probe setup and is split into a strong pump and weak probe with the intensity ratio of pump to probe larger than 10. The focused spot size of the pump and probe is about 50 μm in diameter and overlapped on sample. The pump and probe are perpendicularly polarized so that a polarization analyzer can be placed in front of photodetector to filter out the scattered pump light into the probe. The pump beam is modulated at a frequency of about 1.13 kHz by an optical chopper whose reference output synchronizes a lock-in amplifier which measures transient transmission change of the graphene induced by pump pulses.

3. Results and discussion

3.1. *Characterization of graphene grown by CVD*

A typical Raman spectrum is plotted in Fig. 1(a), and shows that the 2*D* peak is two times more intense than *G* peak, which implies that the graphene is monolayer. *D* peak is hardly observed, which imply the monolayer graphene has less defects [23]. G peak appears at 1587 cm^{-1}, which implies that the sample has a Fermi level of ~0.24 eV according to the doped density dependence of the position of G peak [23].