Thickness dependent hot-phonon effects observed by femtosecond mid-infrared luminescence in graphene

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Abstract: Femtosecond luminescence of graphene and graphite is studied from near- to mid-infrared regions. Remarkable reduction of lifetime at 0.3 eV in mono- and bi-layer graphenes is found, indicating carrier cooling due to interaction with substrate.
OCIS codes: 160.4236 Nanomaterials; 260.3800 Luminescence; 260.7120 Ultrafast phenomena

1. Introduction

Among the carbon-based materials, graphene is most attractive in applications to high speed electronics such as field effective transistors, single electron transistors and optical sensors, because it has a unique symmetric linear dispersion for electron and hole, and high carrier mobilities. For these applications, interaction of the electrons with phonons is important, because the optical response is limited by cooling of the carriers. Transport property is also dependent on the speed of cooling of the hot carriers. From this view point, the dynamics of high energy electrons and coupled phonons have been investigated with various experimental methods, such as transient absorption [1], reflectance[2], anti-Stokes Raman scattering [3], photoelectrons[4,5], and luminescence[6,7]. In most of the reports, the response of photoexcited electrons (holes) has a fast (order of 100 fs) and a slow component ranging from 1.5 to 3 ps. The time constants strongly depends on the observation photon energy, excitation fluence, thickness (layer number), and sample condition. Large difference in the time constant has been reported for free standing and substrate-supported graphenes.

In most of the transient absorption measurements, the responses are observed at single energy in relatively high energy region (typically from 1 to 1.6 eV). Wider range measurements have been performed by luminescence between 1.5 and 3.5 [6] or between 0.7 and 1.4 eV [7]. Time and angle resolved photoemission spectra from -0.5 to 1.5 eV (measured from Fermi energy) including Dirac point has been reported recently [5]. However, in the last case, thickness dependence have not been reported. In spite of these efforts, the reported lifetimes are not consistent each other and especially the thickness dependence is controversial.

To understand the whole picture of photo-excited electron dynamics, it is important to observe the response in a wide energy range especially at low energies close to Dirac point. In this report, we observed luminescence down to 0.3 eV, corresponding to 0.15 eV electron, with a time resolution of 170 fs. The result shows a considerable thickness dependence of the carrier lifetime at low energies.

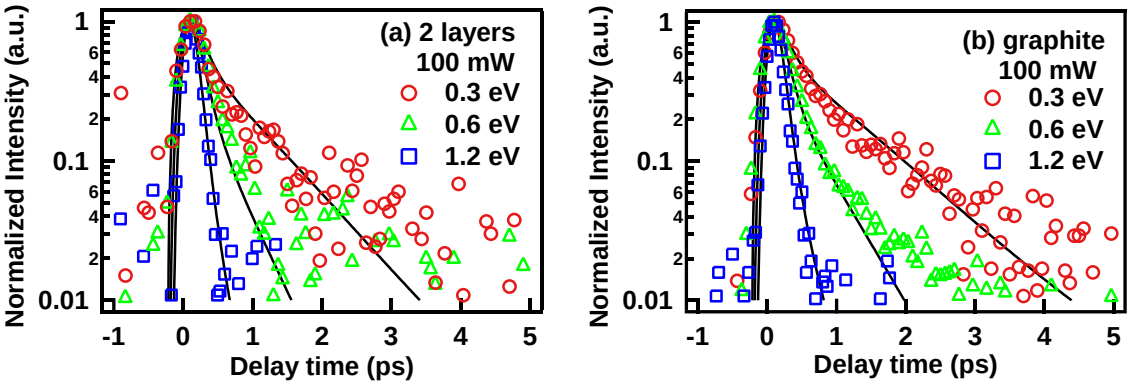

Fig.1 Time evolution of the luminescence intensity in bi-layer graphene (a) and graphite (b) observed at 0.3, 0.6, and 1.2 eV.

2. Experiment

We used mono-, bi- and 6-8-layer graphene sheets purchased from ACS MATERIAL®. The graphene sheets are transferred on to fused silica substrates. For a reference we measured also HOPG graphite.

The sample was excited at 1.57 eV (790 nm), by 70 fs pulses at a repetition rate of 200 kHz, and the infrared luminescence signal was up-converted to visible light and analyzed by a double grating monochromator and detected with a photon counting system.

3. Results and Discussion

Photon energy dependences of the decay profiles in bi-layer graphene and graphite under relatively high excitation fluence are shown in Fig. 1(a) and (b), respectively. In graphite, the lifetime becomes longer at lower photon energy as reported in ref. [8]. In the case of bi-layer graphene, however, the lifetime at 0.3 eV is not so long as that in graphite, while the lifetime at 1.2 eV is almost the same. Elongation of the lifetime at lower energy is ascribed to slower decay of electron population at lower energy, as predicted by Fermi-Dirac distribution assuming cooling down of the electron system via optic phonons.

Luminescence signals from graphenes with different thickness are shown in Fig. 2(a). At the lowest energy 0.3 eV, the thickness dependence is most clearly seen, that is, the lifetime in mono-layer graphene is roughly one half of that in graphite, while that of 6-8 sample is almost the same as that of graphite.

We try to understand these observation in terms of the two-temperature model [7]. We assume that the energy of the electron system is transferred to the 0.2 eV optic phonon (G mode) as the first step and that the energy of the hot optic phonon is dissipated to the large heat bath within the graphene sheet. The calculated curves for graphite are shown in Fig. 1(b) by solid lines, which are in good agreement with experiment. Then the fast decays in bi-layer graphene are reproduced simply by adding a path from the electron system to the optic phonons of the substrate, having an infinite heat capacity. This suggests that the interaction between the hot carriers and the substrate is the main cooling mechanism in silica-supported graphene as proposed in ref. [3].

Another significant difference between graphene and graphite is the excitation fluence dependence of the peak intensity. Figure 2(b) shows the fluence dependence of the peak intensity evaluated around 100fs. At 1 eV, it has square dependence in graphite, while it has nearly linear dependence in bi-layer graphene. This suggests existence of some mechanism which suppresses the initial electron temperature in graphene supported by silica. This is likely to be ascribed to direct interaction of the electrons with the substrate.

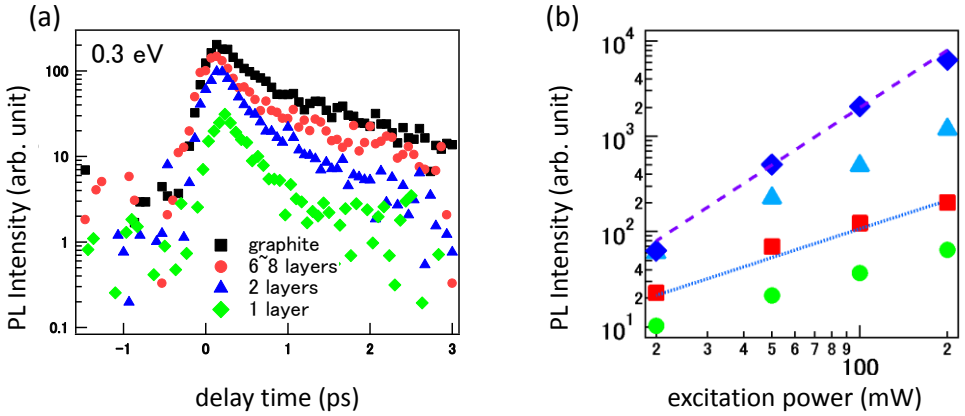

Fig. 2 (a) Thickness dependence of the luminescence decay profiles observed at 0.3 eV. Data for 1, 2 and 6-8 layers graphene and for graphite are shown. (b) Excitation fluence dependence of the luminescence peak intensity (around 100 fs) for bi-layer 0.3 eV(circle), graphite 0.3eV(square), bi-layer 1.0 eV(triangle) and graphite 1.0eV(diamond). Dotted and dashed lines correspond to linear and square dependence.

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