Femtosecond UV-pump/visible-probe measurements of carrier dynamics in stacked graphene films

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The transient differential transmission (ΔT/T) spectra of graphene were obtained from 380 (3.3 eV) to 670 nm (1.9 eV). The intraband carrier equilibration by carrier–carrier scattering occurred within 60 fs. The subsequent carrier relaxation process was governed by carrier-optical phonon scattering and had linear dependence on the probe photon energy (E_p); lifetimes ranged from 180 to 90 fs for E_p from 2.1 to 2.8 eV. Negative ΔT/T signals in kinetic curves were discussed and assigned to thermal diffusion and shrinkage of band separation caused by lattice heating. © 2010 American Institute of Physics. [doi:10.1063/1.3504704]

Graphene is a two-dimensional atomic layer of carbon atoms arranged into a honeycomb crystal structure. Since its discovery in 2004,1 the unique electronic and optical properties have aroused a great deal of interest in both fields of fundamental physics and applications.2 Those properties are related to the energy band structure of graphene.3 By use of angle-resolved photoemission spectroscopy it was experimentally observed that both conical valance and conduction bands converged at the K point (Dirac point) in momentum space,4 in agreement with theoretical calculations.5,6 This peculiar band structure makes the charge carriers (electron and hole) behave like massless relativistic particles (Dirac fermions) which are governed by the Dirac equation.3 Therefore, it is very attractive to uncover the carrier dynamics in graphene. In 2007, Butcher et al.7 reported the calculated relaxation dynamics of photon-excited electrons in graphene. Since 2008, studies on the carrier dynamics by using ultrafast pump-probe8–16 and Z-scan16,17 techniques have made great progress. Observed decay times from 8 fs (Ref. 17) to more than 10 ps (Refs. 9 and 10) were assigned to various relaxation processes such as carrier–carrier (c–c) scattering,8,16,17 carrier–phonon scattering,8–15 phonon–phonon scattering,15 and electron–hole recombination.10 However, those assignments of lifetimes remain controversial. Meanwhile, most previous measurements8–17 on carrier dynamics focused on the limited region (within ±1 eV) around the Dirac energy. In contrast, the dynamics in the higher energy band has not caused sufficient attention.

In the present work, we report UV pump/visible probe spectroscopic studies of the carrier dynamics in stacked graphene films. The transient spectra of differential transmission (ΔT/T) were obtained from 380 (3.3 eV) to 670 nm (1.9 eV) and the carrier kinetics was also continuously acquired in the region from 2.1 to 2.8 eV. By fitting rise, decay and negative data in the transmission kinetics, we found three time constants and accordingly assigned to thermalization due to c–c scattering and initial carrier cooling, carrier–optical phonon (c–op) scattering, and lattice-heating effect in graphene.

Here, graphene was grown by using low-pressure chemical vapor deposition (LPCVD) (Ref. 18) and transferred onto quartz substrate. Eight layer graphene films were stacked layer by layer on quartz for the sake of gathering stronger optical response than that from monolayer. For pump-probe measurements, the output of titanium-sapphire (Legend Elite, Coherent) regenerative amplifier seeded by an oscillator (Micra, Coherent) was used as a pulse laser source; wavelength 800 nm, pulse width 65 fs, pulse repetition rate 1 kHz, and average power 3.5 W. The main part, 90%, of the radiation was converted into the UV (350 nm) by use of optical parametric oscillator (Topas, Light Conversion) with following second- and fourth-harmonic generation that was used as pump pulse. The remaining 10% was used to generate white light continuum in CaF2 plate, i.e., probe pulse. For obtaining the transient ΔT/T spectra, chirp correction was carried out by utilizing the coherent artifact signals from the quartz substrate.19 The errors of obtained time constants are within 10%. The full-width-half-maximum of instrument response function, taken from the pump-probe cross-correlation signal in quartz, was 100 ± 10 fs.

Figure 1 shows the transient differential transmission spectra of stacked graphene films on quartz measured at different delay times after 350 nm excitation. The inset indicates the linear band structure and pump/probe related optical transitions in graphene. In this measurement, we pumped with the photon energy of 3.55 eV and probed with E_p from 1.9 to 3.3 eV. The induced increase in differential transmission ΔT/T during most of probed region, i.e., saturation of absorption due to bleaching, was found to proceed not instantaneously, however, within 60 fs. And then most of non-equilibrium carriers departed from these probed bands before 1 ps. No obvious change in transmission was observed at probe energies above 3 eV that indicated the depopulation of carriers at higher energy levels, especially close to the pumped level, was much faster than that at lower energy levels. The temporal evolution of ΔT/T reflects the dynamic

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distributions of carriers occupying in probed electronic bands, being similar to the theoretical calculations.19–20

Figure 2 presents transmission kinetics of the stacked graphene sample at following three probe wavelengths: 441, 515, and 598 nm. Deconvolution-fit processes of kinetic curves resulted in following two time components: \( \tau_{\text{rise}} = 50–70 \) fs and \( \tau_{\text{decay}} = 90–180 \) fs. The fast rise time originates from two carrier dynamic processes of thermalization due to c–c scattering and initial phonon-mediated carrier cooling. The decay time of \( \Delta T/T \) is mainly due to c–op scattering in graphene. In detail, \( \tau_{\text{rise}} \) represents the time when the maximum bleaching happens at each probed energy level. During this time, the c–c scattering has a predominant responsibility for the formation of quasi-equilibrium distribution of hot carriers.21 Intravalley (I–phonons) and intervalley (K–phonons) scattering processes,22 including phonon modes of \( \Gamma-E_{2g,LO}, \Gamma-E_{2g,TO}, K-A_1' \), and \( K-E' \), have important contributions to the decay time \( \tau_{\text{decay}} \). According to previous studies,21,22 hot carriers have strong coupling to \( K-A_1' \), \( \Gamma-E_{2g,LO} \), and \( \Gamma-E_{2g,TO} \) modes, for energy dissipation. Several publications report on the ultrashort kinetics obtained from pump-probe measurements.8,11,15,16 Time constants of \(<200 \) fs at \( \lambda_{\text{probe}} = 780 \) nm,21 in agreement with our results, were considered to be caused by c–op scattering. Time constants of 200–300 fs at \( \lambda_{\text{probe}} = 1300 \) nm (Ref. 11) due to carrier cooling agree well with extrapolation of our data to infrared (Fig. 3). In Refs. 8 and 16, decay times of 70–120 fs and 130–330 fs, respectively, at \( \lambda_{\text{probe}} = 780–790 \) nm were assigned to c–c scattering.

Figure 3 shows dependence of rise and decay times versus the probe photon energy. The \( \tau_{\text{rise}} \) is within 90 fs over all probed regions, which indicates the processes of carrier thermalization and initial intraband relaxation occur in a wide range (at least, \( \Delta E_{\text{pr}} = 1.4 \) eV) after photocexcitation. Further, rise times in lower \((2.1–2.3 \) eV) and higher \((2.5–2.8 \) eV) \( E_{\text{pr}} \) regions are about or less than 60 fs. Therefore, the time constant of carrier equilibration mainly due to c–c scattering should be \(<60 \) fs which is limited by our resolution. In other studies on c–c scattering in graphene21 and graphite,25,26 ultrafast time constants of, respectively, 8 fs and 13 fs have been claimed.

The longest measured decay time \( \tau_{\text{decay}} \) is 180 fs which arises from c–op scattering at the energy level of 1.05 eV above and below the Dirac energy. It is clear that the decay time has a decreasing tendency down to 90 fs at 1.4 eV from the Dirac energy. Being analogous to semiconductors, the electrons at the lower excited level live longer compared with the ones at the higher energy level. There is a significant feature for decay times at different probe energies; the data can be well fitted by a linear function. That seemingly implies the decay time resulted from c–op scattering being inversely proportional to the electron energy in the range of \( E = 1.05–1.4 \) eV. In graphite, similar dependence was found at smaller energies of \( E = 0.65–0.9 \) eV.21

Recently, it has been demonstrated that graphene can be used as a saturable absorber for mode-locking of ultrafast lasers in infrared; 1565 nm,24 1576 nm,25 1559 nm,26,27 and 1064 nm.27 According to the transient absorption data above, we propose that graphene can serve as a saturable absorber in the visible, 450–670 nm.

In addition to the positive signals in decay curves (Fig. 2), negative “tails” of kinetics were observed at longer delay times (100 ps) between pump and probe pulses (Fig. 4). The recovery time constant of this negative “tail” is 60 ps. Similar phenomena have also been observed in graphene21 and graphite.22,28 Two factors were considered to contribute as follows: (i) the shift in Fermi level induced by doping; (ii) lattice heating effect. In 2008, Sun et al.29 reported the negative \( \Delta T/T \) signal in epitaxial graphene on SiC and they attributed it to the highly doped layers where the heating of the
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