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

Jingzhi Shang,[1] Zhiqiang Luo,[1,2] Chunxiao Cong,[1] Jianyi Lin,[2] Ting Yu,[1,3,a)] and Gagik G. Gurzadyan[1,4,a)]

[1]*Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371*
[2]*Applied Catalysis, Institute of Chemical and Engineering Sciences, Singapore 627833*
[3]*Department of Physics, Faculty of Science, National University of Singapore, Singapore 117542*
[4]*Department Chemie, Technische Universität München, Garching 85748, Germany*

The transient differential transmission ($\Delta T/T$) 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_{pr}); lifetimes ranged from 180 to 90 fs for E_{pr} from 2.1 to 2.8 eV. Negative $\Delta T/T$ 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.[4] Therefore, it is very attractive to uncover the carrier dynamics in graphene. In 2007, Butscher *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-probe[8–16] and Z-scan[16,17] 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 measurements[8–17] 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 ($\Delta T/T$) 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 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 CaF_2 plate, i.e., probe pulse. For obtaining the transient $\Delta T/T$ 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_{pr} from 1.9 to 3.3 eV. The induced increase in differential transmission $\Delta T/T$ 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 nonequilibrium 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 $\Delta T/T$ reflects the dynamic

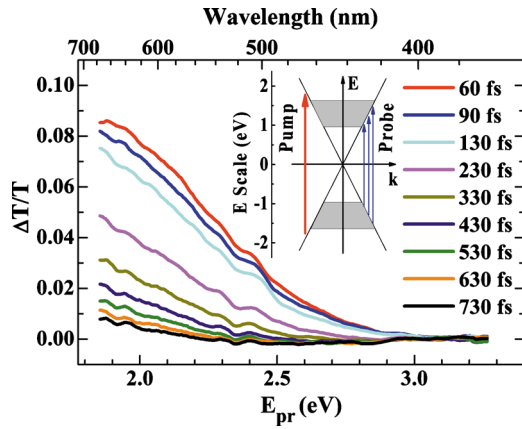a)Electronic addresses: yuting@ntu.edu.sg and gurzadyan@ntu.edu.sg.

FIG. 1. (Color online) Transient differential transmission spectra of stacked graphene films on quartz (λ_{exc}=350 nm). Inset: electronic band structure of graphene and pump/probe configuration.

FIG. 3. (Color online) Decay and rise times vs the probe photon energy. The linear fit of decay times is denoted by the solid line.

distributions of carriers occupying in probed electronic bands, being similar to the theoretical calculations.[7,20]

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: τ_{rise} =50–70 fs and τ_{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, τ_{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 quasiequilibrium distribution of hot carriers.[21] Intravalley (Γ-phonons) and intervalley (K-phonons) scattering processes,[22] including phonon modes of Γ-$E_{2g,LO}$, Γ-$E_{2g,TO}$, K-A_1', and K-E', have important contributions to the decay time τ_{decay}. According to previous studies,[7,23] hot carriers have strong coupling to K-A_1', Γ-$E_{2g,LO}$, and Γ-$E_{2g,TO}$ 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 λ_{probe}=780 nm,[15] in agreement with our results, were considered to be caused by c–op scattering. Time constants of 200–300 fs at λ_{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 λ_{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 τ_{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, ΔE_{pr}=1.4 eV) after photoexcitation. Further, rise times in lower (2.1–2.3 eV) and higher (2.5–2.8 eV) E_{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 graphene[17] and graphite,[21] ultrafast time constants of, respectively, 8 fs and 13 fs have been claimed.

The longest measured decay time τ_{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] and 1064 nm.[27] According to the transient absorption data above, we propose that graphene can serve as a saturable absorber also 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 graphene[9] and graphite.[21,28] 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.*[9] 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
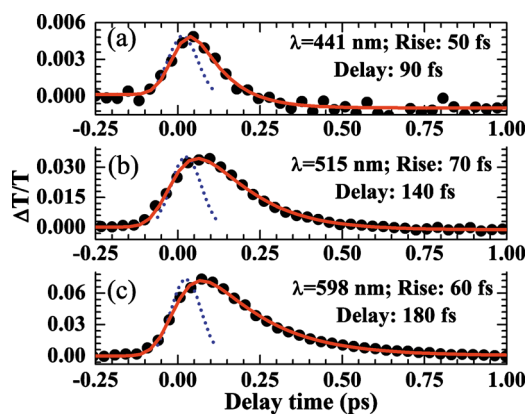

FIG. 2. (Color online) Transient differential transmission spectra for stacked graphene films on quartz as a function of pump-probe delay at (a) 441, (b) 515, and (c) 598 nm. Dotted curves: instrument response function.
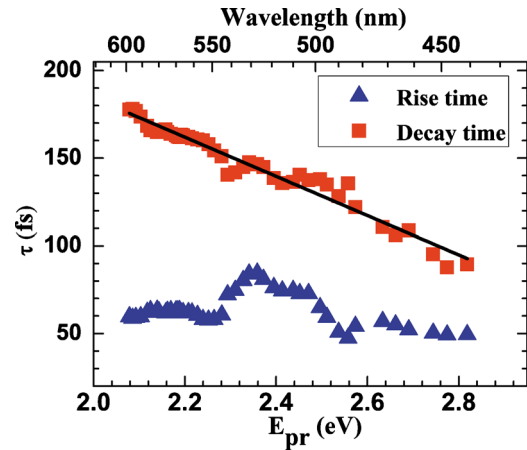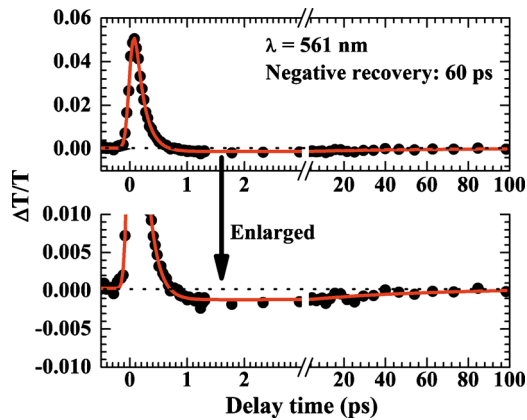
FIG. 4. (Color online) Measured transmission kinetics at 561 nm for the stacked graphene films on quartz.

electron plasma reduced the occupation probability. In particular, the signal needed that the probe range was lower than the Fermi level of graphene.[9] As a result, our negative signal cannot be derived by this factor as the probed energy level is high and far from the Fermi level. We explain are prone to explain the negative signal in terms of thermal diffusion and shrinkage of band separation[21,28] driven by lattice heating from the carrier relaxation process. Particularly, Seibert *et al.*[28] observed the redshift in partial reflectivity spectrum of highly oriented pyrolytic graphite caused by UV pump pulses. It should also be mentioned that for nonfreestanding samples the contribution of substrate, such as charge transfer[11,20] between graphene and substrate, cannot be fully excluded which may also result in negative signals of $\Delta T/T$.

To sum up, ultrafast carrier dynamics of stacked graphene films was studied in visible spectral region by using 65 fs, 350 nm pump, and visible probe pulses. The transient differential transmission spectra were obtained from 380 (3.3 eV) to 670 nm (1.9 eV); in the range of 450–670 nm, strong increase in transmission, i.e., bleaching, was detected. Observed transient $\Delta T/T$ spectra visually reflected temporal evolution of carrier population in probed electronic band. The intraband carrier equilibration by c–c scattering was found to proceed within 60 fs. Afterwards, the intraband carrier relaxation was dominated by c–op scattering. The process of c–op scattering showed apparent dependence on the probe wavelength, where the decay time linearly decreased from 180 to 90 fs with the increase in E_{pr} from 2.1 to 2.8 eV. Moreover, it was found that thermal diffusion and shrinkage of band separation, caused by lattice heating, gave rise to a negative $\Delta T/T$ signal with a lifetime of 60 ps. Based on previous reports[24–27] and current studies on carrier dynamics in graphene, we suggest that the lasing range of ultrafast graphene mode-locked lasers can be extended to the visible region.

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science **306**, 666 (2004).
[2] A. K. Geim and K. S. Novoselov, Nature Mater. **6**, 183 (2007).
[3] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. **81**, 109 (2009).
[4] A. Bostwick, T. Ohta, T. Seyller, K. Horn, and E. Rotenberg, Nat. Phys. **3**, 36 (2007).
[5] S. Reich, J. Maultzsch, C. Thomsen, and P. Ordejón, Phys. Rev. B **66**, 035412 (2002).
[6] B. Partoens and F. M. Peeters, Phys. Rev. B **74**, 075404 (2006).
[7] S. Butscher, F. Milde, M. Hirtschulz, E. Malic´, and A. Knorr, Appl. Phys. Lett. **91**, 203103 (2007).
[8] J. M. Dawlaty, S. Shivaraman, M. Chandrasekhar, F. Rana, and M. G. Spencer, Appl. Phys. Lett. **92**, 042116 (2008).
[9] D. Sun, Z.-K. Wu, C. Divin, X. B. Li, C. Berger, W. A. de Heer, P. N. First, and T. B. Norris, Phys. Rev. Lett. **101**, 157402 (2008).
[10] P. A. George, J. Strait, J. Dawlaty, S. Shivaraman, M. Chandrashekhar, F. Rana, and M. G. Spencer, Nano Lett. **8**, 4248 (2008).
[11] R. W. Newson, J. Dean, B. Schmidt, and H. M. van Driel, Opt. Express **17**, 2326 (2009).
[12] J. Wang, Y. Hernandez, M. Lotya, J. N. Coleman, and W. J. Blau, Adv. Mater. (Weinheim, Ger.) **21**, 2430 (2009).
[13] H. Choi, F. Borondics, D. A. Siegel, S. Y. Zhou, M. C. Martin, A. Lanzara, and R. A. Kaindl, Appl. Phys. Lett. **94**, 172102 (2009).
[14] H. Wang, J. H. Strait, P. A. George, S. Shivaraman, V. B. Shields, M. Chandrashekhar, J. Hwang, F. Rana, M. G. Spencer, C. S. Ruiz-Vargas, and J. Park, Appl. Phys. Lett. **96**, 081917 (2010).
[15] L. Huang, G. V. Hartland, L. Q. Chu, Luxmi, R. M. Feenstra, C. Lian, K. Tahy, and H. Xing, Nano Lett. **10**, 1308 (2010).
[16] S. Kumar, M. Anija, N. Kamaraju, K. S. Vasu, K. S. Subrahmanyam, A. K. Sood, and C. N. R. Rao, Appl. Phys. Lett. **95**, 191911 (2009).
[17] G. Xing, H. Guo, X. Zhang, T. C. Sum, and C. H. A. Huan, Opt. Express **18**, 4564 (2010).
[18] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, and R. S. Ruoff, Science **324**, 1312 (2009).
[19] M. Lorenc, M. Ziolek, R. Naskrecki, J. Karolczak, J. Kubicki, and A. Maciejewski, Appl. Phys. B: Lasers Opt. **74**, 19 (2002).
[20] M. Richter, A. Carmele, S. Butscher, N. Bücking, F. Milde, P. Kratzer, M. Scheffler, and A. Knorr, J. Appl. Phys. **105**, 122409 (2009).
[21] M. Breusing, C. Ropers, and T. Elsaesser, Phys. Rev. Lett. **102**, 086809 (2009).
[22] J. Maultzsch, S. Reich, C. Thomsen, H. Requardt, and P. Ordejo'n, Phys. Rev. Lett. **92**, 075501 (2004).
[23] S. Piscanec, M. Lazzeri, F. Mauri, A. C. Ferrari, and J. Robertson, Phys. Rev. Lett. **93**, 185503 (2004).
[24] Q. Bao, H. Zhang, Y. Wang, Z. Ni, Y. Yan, Z. X. Shen, K. P. Loh, and D. Y. Tang, Adv. Funct. Mater. **19**, 3077 (2009).
[25] H. Zhang, D. Y. Tang, L. M. Zhao, Q. L. Bao, and K. P. Loh, Opt. Express **17**, 17630 (2009).
[26] Z. Sun, T. Hasan, F. Torrisi, D. Popa, G. Privitera, F. Wang, F. Bonaccorso, D. M. Basko, and A. C. Ferrari, ACS Nano **4**, 803 (2010).
[27] W. D. Tan, C. Y. Su, R. J. Knize, G. Q. Xie, L. J. Li, and D. Y. Tang, Appl. Phys. Lett. **96**, 031106 (2010).
[28] K. Seibert, G. C. Cho, W. Kütt, H. Kurz, D. H. Reitze, J. I. Dadap, H. Ahn, and M. C. Downer, Phys. Rev. B **42**, 2842 (1990).