

High-Frequency Coherent Phonons in Graphene on Silicon Substrate

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(Received February 9, 2011; accepted February 27, 2011; published online March 14, 2011)

High-frequency coherent vibrations have been investigated in graphene on silicon substrate through pump-probe anisotropic reflectivity spectroscopy with 7.5 fs laser pulses. The coherent phonons of both intralayer C=C stretching mode (G-mode) and disorder-induced mode (D-mode) are clearly observed even in monolayer graphene. The frequency of the G-mode shifts to higher frequency with decreasing the number of graphene layers, whereas the D-mode does not show such hardening. We also find that the D-mode softens upon photoexcitation and then shifts to higher frequency during the relaxation process. The different behavior in the frequency-shift between the G- and D-modes is discussed.

Graphene, a single sheet of carbon atoms, has attracted much interest in both fundamental physics and applications, since the discovery of graphene by Novoselov *et al.* [1]. Electrons in an ideal graphene behave like the massless Dirac fermions [2], leading to many interesting electronic properties such as an anomalous quantum Hall effect, ballistic electron transport and high carrier mobility more than $100,000 \text{ cm}^2/\text{Vs}$ at room temperature [3-5]. Owing to these unusual properties, graphene is a promising candidate for new class of electronic devices beyond the scaling-limit of silicon devices. For fabrication of graphene, there are two approaches: micromechanical cleavage [1] and epitaxial growth on semiconductor substrates such as SiC [5,6]. Although the cleavage method produces high-quality graphene flakes, the exfoliated graphene is not practical because of its limited size and less-productivity. The epitaxial graphene on SiC substrate also has problems for the industrial purpose: limited size of SiC wafers and incompatibility with mature silicon technology. To overcome these limitations, recently, the GOS (graphene on Si substrate) method has been proposed as one of the promising way to form high-quality graphene films on large-scale Si wafers [7].

To characterize the structure of graphene, steady-state Raman spectroscopy is commonly utilized [6,8-11]. Raman spectroscopy also allows to elucidate the electron-phonon coupling relevant to the massless Dirac fermions [12,13]. For example, the G-band associated with an intralayer C=C stretching mode ($\sim 1580 \text{ cm}^{-1}$) stiffens and sharpens with increasing charge density, while the G' (2D) band associated with a two-phonon state ($\sim 2700 \text{ cm}^{-1}$) in which each phonon has a large wavevector shows a different response [12-14]. Since the dephasing and time-dependent frequency-shift of these modes can be directly revealed, ultrafast measurements on high-frequency coherent phonons interacting with charges is indispensable for further understanding the electron-phonon interactions in graphene.

However, contrasting to other carbon materials such as graphite and carbon nanotubes [15-17], dynamics of coherent phonons in graphene has not been reported to date. It is probably because the transient signals coming from a few layers of the exfoliated graphene with tiny small area are expected to be very weak. In this paper, we report the first measurements on high-frequency coherent vibrations in graphene through transient anisotropic reflectivity measurements with 7.5 fs laser pulses. Taking advantage of large homogeneous area in GOS coupled with sensitive ultrafast measurements, we clearly observed the high-frequency coherent phonons even in monolayer graphene.

The SiC thin films with typical thickness of 80 nm were first grown on p-type Si substrate by gas-source molecular-beam epitaxy. Then the films were uniformly annealed by resistive heating to graphitize SiC surface. The detail of the sample preparation is described elsewhere [7,18,19]. The characterization of GOS was carried out by transmission-electron microscopy (TEM) and steady-state microscopic Raman spectroscopy. From these measurements, the number of graphene layers n was also determined.

High-frequency coherent vibrations were investigated with pump-probe transient anisotropic reflectivity measurements. We use a Ti-sapphire oscillator with pulse duration of 7.5 fs, repetition rate of 80 MHz, and center wavelength of 800 nm as a light source. The output laser pulses from the oscillator were divided into two beams; one is used as pump beam to generate coherent vibrations, and the other as probe beam to observe the high-frequency coherent phonons. During the experiments, the pump intensity was kept to 30 mW (0.1 mJ/cm^2) which is much lower than the threshold intensity of the sample damage, while the probe intensity was one order of magnitude smaller than the pump intensity. We also confirmed that the observed transient signal follows the linear dependence of the pump

intensity. An optical shaker with scanning range of 15 ps was placed along the optical path for the pump beam, and rapidly scanned with 20 Hz. The probe beam reflected from the sample surface was then measured with electro-optic (EO) sampling method [20]. Using the EO sampling method with typical accumulation time of 1 hour, the reflectivity change ($\Delta R/R$) less than 10^{-6} was successfully detected. All the measurements were performed at room temperature.

Figures 1(a) and 1(b) show the typical transient reflectivity change of GOS with 4 graphene layers and its Fourier transformed (FT) spectrum. Not only the strong electronic response at the time origin ($t=0$) but also the coherent oscillation of the LO-phonon relevant to Si substrates (~ 65 fs) [21] are clearly observed in time domain. In addition to these signals, the high-frequency oscillations are also observed at the early stage as shown in the inset. In the FT spectrum, we could see a strong peak at 15.6 THz coming from Si substrate and the two weak peaks at 40~50 THz. To visualize these high-frequency coherent vibrations clearly, the strong electronic response as well as the coherent oscillation from Si substrate is analytically subtracted; for the subtraction process, the transient reflectivity changes obtained are once transformed to the FT spectra in frequency domain, and then both the low-frequency mode and the electronic response are filtered out. Figure 1(c) shows the transient reflectivity changes of GOS after the filtering for different number of graphene layers n . As comparison, that of highly-oriented pyrolytic graphite (HOPG) is also shown. The intensity of the reflectivity changes becomes weak with decreasing n . The HOPG shows only one oscillatory component with a long dephasing time (~ 1.0 ps), while the GOS indicates an apparent modulation of oscillatory components with a fast dephasing time less than 1 ps. The FT spectra of the high-frequency components for different number of layers are shown in Fig.

1(d). The two Raman peaks are located at ~ 47 THz and ~ 40 THz; the Raman peak at ~ 47 THz originates from the G-mode which is well known in graphite, while the Raman peak at ~ 40 THz is due to the disorder-induced mode (D-mode) which is commonly observed in many sp²-bonded carbons [16,22]. As far as we know, this is the first observation of the high-frequency coherent phonons in graphene.

Figures 2(a) and 2(b) show the observed frequencies and dephasing rates of the G- and D-modes as a function of $1/n$. The frequency of the D-mode is almost independent of the number of layers. On the other hand, that of the G-mode linearly shifts to higher frequency with increasing $1/n$, which indicates hardening of the G-mode. The frequency of the G-mode in monolayer GOS shows a blue-shift of 0.8 THz (26 cm^{-1}) relative to that in HOPG. The same behavior is also reported on steady-state Raman measurements both in mechanically transferred thin flakes on Si substrate [8] and in epitaxial graphene on SiC(0001) substrate [11]. As comparison, here, the frequency-shift of the G-mode in epitaxial graphene is plotted by open triangles in Fig. 2(a). The observed frequency-shift of the G-mode is in quite good agreement with that reported by Röhrl *et al.* [11].

It is well known that the phonon frequencies of graphene are affected either by mechanical strain [6,11], or by charge that comes from the Kohn anomaly [12,13,23]. Röhrl *et al.* claim that the blue-shift of the G-mode is mainly due to compressive strain occurring when the sample is cooled down from annealing temperature to room temperature. Since the blue-shift observed in this study is almost the same value obtained by others [6,11] and our sample may have strain between graphene and Si substrate, the observed hardening of the G-mode with increasing $1/n$ mostly comes from strain. The dephasing rate of the HOPG is about 1 ps^{-1} . With increasing $1/n$, both the dephasing rates of the G- and D-modes are

increased. Since the D-mode is affected by defects more than the G-mode, the dephasing rate of the D-mode is larger than that of the G-mode. The observed dephasing time is comparable with the ultrafast relaxation time of photoexcited carriers recently reported [24-26].

The advantage of our ultrafast transient spectroscopy is to observe directly the time evolution of phonon frequencies, that is, the chirp characteristic. Since the pump laser pulse produces carriers (electron-hole pairs), the frequency-shift of high-frequency coherent phonons by the photoexcited carrier doping is expected, whose information is key to understand the electron-phonon interaction contributing to the Kohn anomaly. Figure 3 shows the time-frequency two-dimensional map in GOS with 4 graphene layers obtained from time-windowed Fourier transformation. The width of the Hanning time-window was set to 0.2 ps. The G-mode does not show the clear frequency-shift, while the D-mode shifts to higher frequency with time after 0.2 ps. Recently, Ishioka *et al.* observed that the phonon frequency of the G-mode in HOPG shows the blue-shift (~ 0.2 THz) upon photoexcitation and relaxes to the stationary value within a few picoseconds [15]. The G-mode of the carrier-doped graphene also stiffens with increasing carrier density [12,13]. Judging from the first-principle calculations, this behavior is considered to be due to the decoupling of the electron-phonon interaction by non-equilibrium electron-hole plasma induced by pump pulses [15]. Because the excitation density (0.1 mJ/cm^2) in this work is much smaller than that in Ref. 15 and the dephasing rate of the G-mode observed in GOS is 3~4 times larger than that in HOPG as shown in Fig. 2(b), the blue-shift of the G-mode might not be observed upon the photoexcitation. On the other hand, we first find that the D-mode shows the huge higher frequency-shift (~ 1.5 THz) with time during the relaxation process as shown in Fig. 3. This behavior could be simply explained as follows; the photoexcited carriers make the bond

weaker (softening), leading to the instantaneous red-shift in frequency (~ 39.5 THz) relative to the stationary value of 40.9 THz [19]. Subsequently the frequency recovers to the stationary value via the relaxation process. The D-mode frequency is highly dispersive due to a k -selective double resonance process [14]. The wide energy distribution of the D-mode phonons contributing to the scattering process induced by ultrashort laser pulses might also affect the time-dependent frequency-shift. Elaborate theoretical calculations are needed for further understanding of the high-frequency coherent phonon dynamics of graphene.

In summary, we have investigated the high-frequency coherent vibrations in graphene on Si substrate with pump-probe reflectivity spectroscopy. Even in monolayer graphene, the high-frequency coherent phonons of both G- and D-modes are clearly observed for the first time. Since the time-domain spectroscopy with ultrashort laser pulses allows to directly observe the ultrafast phonon dynamics, not only the frequency-shift and dephasing rate of the G- and D-modes with the number of graphene layers but also the time evolution of these modes are revealed.

Acknowledgements

We acknowledge Dr. Tohru Shimada for his considerable contributions to buildup the pump-probe reflectivity spectroscopy at the early stage of this work. This work was partly supported by the Grant-in-Aids for Scientific Research (Nos. 20241025, 21104510 and 21310065) from JSPS and MEXT. IK also acknowledges the financial supports for the Special Coordination Funds for Promoting Science and Technology from Japan Science and Technology Agency (JST).

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Figure Captions

Figure 1

(a) Typical transient reflectivity change of GOS sample and (b) its Fourier transformation (FT) spectrum. The data are also shown in the enlarged scale (x50). (c) Transient reflectivity changes of the high-frequency coherent vibrations in GOS and HOPG after subtracting the electronic response and the low-frequency oscillations. The 1L, 3L and 10L denote the number of graphene layers. (d) The FT spectra of the time-domain traces in (c). The red curves are the best fits with Lorentzian functions.

Figure 2

(a) The observed frequencies and (b) dephasing rates of the G- and D-modes as a function of the inverse of the number of graphene layers ($1/n$). As comparison, the frequencies of the G-mode in graphene on epitaxial SiC(0001) substrate reported by Röhrl *et al.* are also shown by open triangles. The broken curves are guides for eyes.

Figure 3

Time-frequency two-dimensional map of the high-frequency coherent phonons in GOS with 4 graphene layers. The broken lines show the frequency-shift of the G- and D-modes. The arrows indicate the stationary values of the G- and D-modes. The width of the Hanning time-window was set to 0.2 ps.

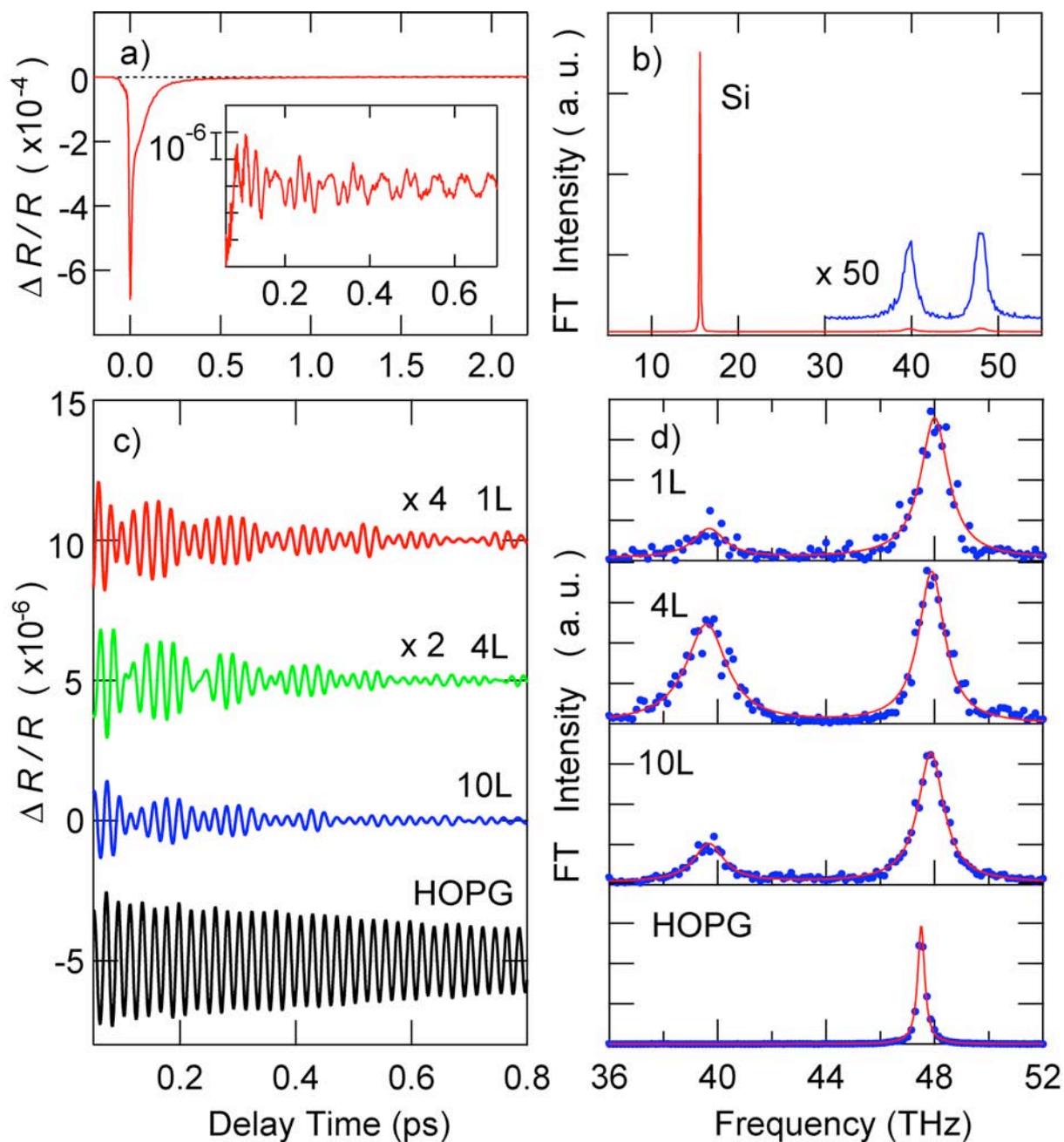


Figure 1: S. Koga *et al.*

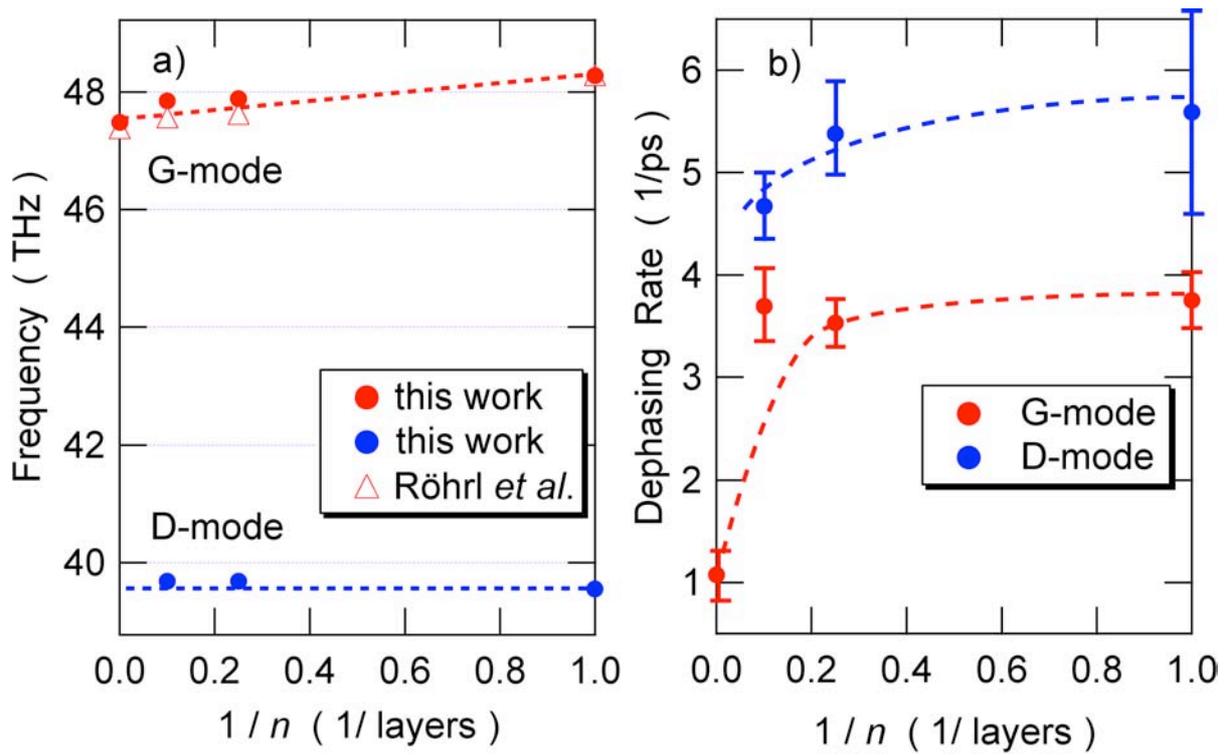


Figure 2: S. Koga *et al.*

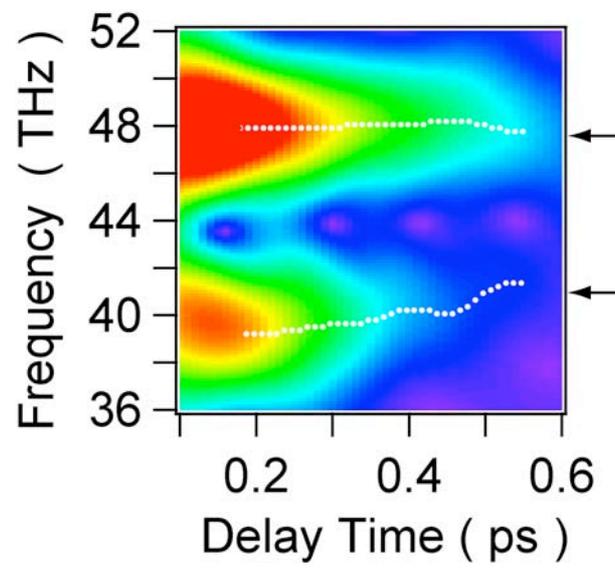


Figure 3: S. Koga *et al.*