AIP | Applied Physics Letters

Coherent optical phonons in diamond

Kunie Ishioka, Muneaki Hase, Masahiro Kitajima, and Hrvoje Petek

Citation: Applied Physics Letters **89**, 231916 (2006); doi: 10.1063/1.2402231
View online: http://dx.doi.org/10.1063/1.2402231
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/89/23?ver=pdfcov
Published by the AIP Publishing

Coherent optical phonons in diamond

Kunie Ishioka,[a] Muneaki Hase,[b] and Masahiro Kitajima
Advanced Nano-Characterization Center, National Institute for Materials Science, Tsukuba 305-0047, Japan

Hrvoje Petek
Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(Received 8 August 2006; accepted 19 October 2006; published online 6 December 2006)

The authors report femtosecond dynamics of the coherent optical phonon of single crystal diamond. Sub-10 fs, 395 nm laser pulses excite 40 THz coherent phonons with an extremely small damping rate (0.15 ps^{-1}). Linear power dependence of the phonon amplitude under off-resonant excitation condition gives a direct evidence for an eletric-field-driven generation mechanism. The coherent phonon generation is noticeably suppressed by doping with nitrogen impurities, in spite of their absorption in the near ultraviolet. The present study demonstrates that a simple pump-probe technique can be a powerful tool for evaluating the ultrafast coherent electronic and lattice dynamics of diamond materials. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2402231]

Diamond is the quintessential covalently bonded crystal with the highest hardness and thermal conductivity among the known materials. It has the widest band gap among the group IV elemental crystals, and thus serves as an ideal insulator with excellent optical properties. Doping of diamond by group III or V atoms turns it to *p*-or *n*-type semiconductor. Development of the chemical vapor deposition growth technique has enabled the fabrication of a UV-light emitting diamond *pn* junction:[1] a key technology for the future development of diamond-based UV lasers. Also, recently it has been demonstrated that diamond with high concentration of B doping undergoes a superconducting phase transition above the liquid helium temperature.[2,3] Although the mechanism for the superconductivity in diamond is under discussion, it is highly probable that electron-phonon interaction plays an essential role. Indeed, electron-phonon interaction in diamond obtained from isotope substitution studies is very strong, much stronger than that for Si and Ge.[4] Nitrogen-related defects in diamond also offer the possibility of room-temperature spin entanglement.[5]

Since early measurements with inelastic neutron scattering, phonon dynamics in diamond have been studied extensively by both experiment and theory.[6] Many other unique properties of diamond such as hardness, very high Debye temperature, and high thermal conductivity are also determined by or deeply related to its phonon spectrum. The frequency and linewidth of the optical phonon of diamond is a widely used measure for evaluating the crystallinity of diamond-related materials. Time-resolved measurements of the coherent optical phonons give a complementary and more detailed information on the femtosecond dynamics of phonons and their coupling with electrons.[7,8] Because of the challenging requirement for ultrabroad laser bandwidth, however, the coherent excitation of C–C bond vibrations has only been demonstrated in molecular systems[9] and, very recently, in carbon nanotubes[10] and graphite.[8] In this letter, we demonstrate the application of simple pump-probe transient reflectivity technique without spectral resolution or phase modulation to detect a very weak signal from the coherent optical phonons in diamond. We offer evidence for its excitation via the nonresonant impulsive stimulated Raman scattering process.

The samples used are synthetic types IIa and Ib diamond single crystal plates, from Sumitomo Electric Hardmetal, oriented to expose the (100) surface. Type IIa is a high purity diamond with nominally no absorption between 225 nm and 2.5 μm, while type Ib has an absorption in the visible and near ultraviolet due to isolated N impurities with concentration of <100 ppm. Pump-probe reflectivity measurements are performed using optical pulses with <10 fs duration, 395 nm wavelength, and 64 MHz repetition rate. Linearly polarized pump and probe beams are focused to a nominally 10 μm spot on the sample with angles of 20° and 5° from the surface normal, respectively. Pump power is varied between 5 and 50 mW (pulse energies 0.1 and 1 mJ/cm^2), while probe power is kept at 2 mW. The pump and probe beams are polarized 90° and 45° with respect to the optical plane, respectively. Anisotropic reflectivity measurements are carried out in the electro-optic sampling configuraion.[7,8] The time delay between pump and probe pulses is scanned at a 20 Hz rate to enable accumulation up to 25 000 scans. Microscopic Raman scattering measurements are performed with a 532 nm light excitation. The nominal spectral resolution is 0.15 cm^{-1}. Extreme care is taken to avoid the heating

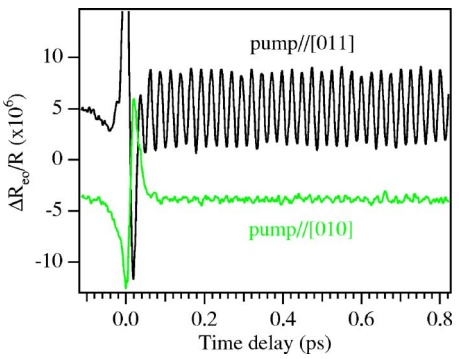

FIG. 1. (Color online) Transient anisotropic reflectivity $\Delta R_{co}/R=(\Delta R_p - \Delta R_s)/R$ of type Ib diamond for different sample orientations. Pump power is 40 mW. Angle between pump and probe polarizations is kept at 45° while the sample is rotated normal to the surface. Traces are offset for clarity.

[a]Electronic mail: ishioka.kunie@nims.go.jp
[b]Present address: Institute of Applied Physics, University of Tsukuba.

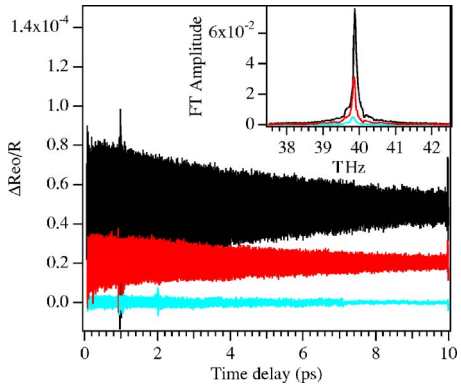

FIG. 2. (Color online) Oscillatory part of the anisotropic reflectivity change of type IIa diamond for pump powers of 5, 20, and 50 mW. Traces are offset for clarity. The inset shows the Fourier-transformed spectra of the oscillatory part.

of the sample during the Raman measurement.

Figure 1 shows the anisotropic reflectivity change $\Delta R_{eo}/R$ of diamond. It consists of an instantaneous electronic response at $t=0$ followed by oscillations with a period of 25 fs, when the pump polarization is parallel to the [110] direction. The frequency of ~40 THz, or ~1330 cm^{-1}, agrees well with the Raman active optical phonon of diamond.[12] In the short time window of Fig. 1, the oscillation is hardly damped. The oscillatory signal essentially vanishes after rotating the sample by 45° within the surface. The sample-orientation dependence is consistent with the off-diagonal Raman tensor of the optical phonons with $\Gamma_{25'}$ symmetry,[13] which has $\cos 2\theta$ dependence for the angle between the electric field of the pump and the [110] direction of the crystal. The polarization angle dependence confirms that Raman scattering process is primarily responsible for the coherent phonon generation, as in other group IV crystals, Si (Ref. 7) and Ge.[11]

Figure 2 compares the $\Delta R_{eo}/R$ signal over more than 400 cycles of the coherent oscillation and its Fourier transformed (FT) spectrum for different pump powers. The oscillation can be fit as a damped harmonic oscillation,

$$\frac{\Delta R_{eo}}{R} = A_0 \exp(-\Gamma t)\sin(2\pi\nu t + \delta), \tag{1}$$

which gives a very large Q factor, $\Gamma\omega \sim 300$. Correspondingly, the linewidth of the FT peak in the inset of Fig. 2 is very narrow. The initial amplitude A_0 obtained from the fit of the $\Delta R_{eo}/R$ signal for the IIa and Ib samples is plotted in Fig. 3 for different pump powers.

One immediately notices that A_0 increases with linear proportion to the pump power, while the other parameters such as Γ and ν remain constant (not shown). Since two or three 3.14 eV photons are required for the indirect (5.48 eV) or direct (7.3 eV) band gap excitation, the linear power dependence clearly indicates the off-resonant nature of the coherent phonon generation. The off-resonant nature is also reflected in the pump-power independent frequency and dephasing rates. Also, the initial phase of the coherent oscillation, $\delta = -161° \pm 39°$, is consistent with the impulsive excitation. These results altogether indicate that the coherent optical phonons are *not* generated by photoexcited carriers *but* driven by electomaginetic field via stimulated Raman scattering. This is in clear contrast with GaN, where the power-dependent dephasing rate attributed the three-photon absorption across the band gap.[14]

We emphasize that the linear power dependence of the phonon amplitude, described above, is observed in type IIa diamond, which has nominally no absorption for 3.14 eV light. An interesting question is whether the doping by impurities can affect the coherent phonon generation by causing, e.g., resonant enhancement of multiphoton interband transition or Fano interference between discrete phonons and doped carrier electron-hole pair continuum? Figure 3 shows a clear-cut answer. The coherent phonon amplitude in type Ib (yellow) diamond shows a linear power dependence, and is noticeably *smaller* than that in type IIa (colorless) sample. This propensity is also observed as the peak height in the Raman spectrum of the optical phonon (last column in Table I), indicating that the apparent suppression of the optical phonon is not transient in nature but is given by the Raman cross section. Unlike B-doped diamond under UV excitation,[15] a Fano-type line shape is not observed for our N-doped sample in the time or frequency domain measurements. Our results suggest virtually no coupling between the optical phonons and the electrons involved in the ionization of the N impurities under present experimental conditions. The yet unexplained role of impurity doping on the suppression of the Raman amplitude will be explored in the future for a wider range of samples.

The dephasing rate (or linewidth) Γ is only slightly but systematically larger in type Ib than type IIa, both in the time-domain and Raman measurements, as summarized in Table I. Our result is consistent with the slight N-concentration dependence of the Raman linewidth,[16] and confirms that the impurities act as scattering centers for the optical phonons. We note that the scattering is not by hot electrons or hot phonons but by static disorder in the lattice periodicity,[17] since Γ is independent of pump power in type Ib as well as type IIa. The present time-domain measurement gives the dephasing rate of 0.145 ± 0.037 ps^{-1} or 1.54 ± 0.39 cm^{-1} for type IIa diamond, which is smaller than the rate of 0.345 ps^{-1} obtained from a four-wave mixing measurement,[18] but close to the average among the scattered

TABLE I. Comparison of the optical phonon parameters obtained from time-domain and Raman measurements. Errors for time-domain measurements are for a single measurement; run-to-run errors for ν and Γ are 0.14 and 0.039 THz, respectively. The spectral resolution for Raman measurements is 0.15 cm^{-1}.

	Time domain				Raman scattering		
	ν		Γ				
Sample	(THz)	(cm^{-1})	(ps^{-1})	(cm^{-1})	Frequency (cm^{-1})	FWHM (cm^{-1})	Peak height (arbitrary unit)
Type IIa	39.84±0.03	1329.0±1.0	0.145±0.037	1.54±0.39	1331.3	1.56	550
Type Ib	40.22±0.01	1341.5±0.5	0.170±0.036	1.81±0.38	1331.3	1.73	100

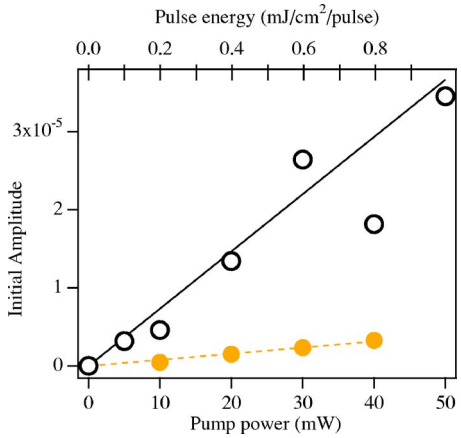

FIG. 3. (Color online) Initial amplitude A_0 of the coherent optical phonon of diamond obtained by the fitting of time-domain data to Eq. (1). Filled and open symbols represent types IIa (colorless) and Ib (yellow) diamonds, respectively. Lines represent linear fits.

experimental Raman linewidths in Ref. 19. We also observe a consistent difference in the phonon frequency in types IIa and Ib diamonds from time-domain measurements, in spite that the Raman shift from the same two samples coincides perfectly.

In summary, we applied a simple pump-probe technique to investigate the ultrafast dynamics of the coherent optical phonons of diamond at 40 THz. The coherent phonon response shows strong sensitivity to doping and therefore provides a powerful method for investigating the ultrafast electron-phonon coupling dynamics in semiconducting and superconducting diamonds.

The authors thank Takeshi Mitani for Raman measurement. This work was supported by KAKENHI 17540305 and 18340093 and NSF CHE-0209706.

[1]S. Koizumi, K. Watanabe, M. Hasegawa, and H. Kanda, Science **292**, 1899 (2001).
[2]E. A. Ekimov, V. A. Sidorov, E. D. Bauer, N. N. Mel'nik, N. J. Curro, J. D. Thompson, and S. M. Stishov, Nature (London) **428**, 542 (2004).
[3]T. Yokoya, T. Nakamura, T. Matsushita, T. Muro, Y. Takano, M. Nagao, T. Takenouchi, H. Kawarada, and T. Oguchi, Nature (London) **438**, 647 (2005).
[4]M. Cardona, Solid State Commun. **133**, 3 (2005).
[5]T. Gaebel, M. Domhan, I. Popa, C. Wittmann, P. Neumann, F. Jelezko, J. R. Rabeau, N. Stavrias, A. D. Greentree, S. Prawer, J. Meijer, J. Twamley, P. R. Hemmer, and J. Wrachtrup, Nat. Phys. **2**, 408 (2006).
[6]J. Kulda, H. Kainzmaier, D. Strauch, B. Dorner, M. Lorenzen, and M. Krisch, Phys. Rev. B **66**, 241202 (2002) and references therein.
[7]M. Hase, M. Kitajima, A. M. Constantinescu, and H. Petek, Nature (London) **426**, 51 (2003).
[8]K. Ishioka, M. Hase, M. Kitajima, L. Wirtz, A. Rubio, and H. Petek (unpublished).
[9]T. Kobayashi, A. Shirakawa, H. Matsuzawa, and H. Nakanishi, Chem. Phys. Lett. **321**, 385 (2000).
[10]A. Gambetta, C. Manzoni, E. Menna, M. Meneghetti, G. Cerullo, G. Lanzani, S. Tretiak, A. Piryatinski, A. Saxena, R. L. Martin, and A. R. Bishop, Nat. Phys. **2**, 515 (2006).
[11]K. Ishioka, M. Kitajima, and K. Ushida, J. Phys. Soc. Jpn. **75**, 084704 (2006).
[12]S. A. Solin and A. K. Ramdas, Phys. Rev. B **1**, 1687 (1970).
[13]W. Hayes and R. Loudon, *Scattering of Light by Crystals* (Wiley, New York, 1978), p. 95.
[14]K. J. Yee, K. G. Lee, E. Oh, and D. S. Kim, Phys. Rev. Lett. **88**, 105501 (2002).
[15]Y. G. Wang, S. P. Lau, B. K. Tay, and X. H. Zhang, J. Appl. Phys. **92**, 7253 (2002).
[16]H. Hanzawa, N. Umemura, Y. Nishida, H. Kanda, M. Okada, and M. Kobayashi, Phys. Rev. B **54**, 3793 (1996).
[17]J. M. Zhang, M. Giehler, A. Göbel, T. Ruf, M. Cardona, E. E. Haller, and K. Itoh, Phys. Rev. B **57**, 1348 (1998).
[18]A. Laubereau, D. von der Linde, and W. Kaiser, Phys. Rev. Lett. **27**, 802 (1971).
[19]M. S. Liu, L. A. Bursill, S. Prawer, and R. Beserman, Phys. Rev. B **61**, 3391 (2000) and references therein.