Frequency comb generation at terahertz frequencies by coherent phonon excitation in silicon

Muneaki Hase1,2*, Masayuki Katsuragawa3, Anca Monia Constantinescu1 and Hrvoje Petek1*

High-order nonlinear light–matter interactions in gases enable the generation of X-ray and attosecond light pulses, metrology and spectroscopy. Optical nonlinearities in solid-state materials are particularly interesting for combining optical and electronic functions for high-bandwidth information processing. Third-order nonlinear optical processes in silicon have been used to process optical signals with bandwidths greater than 1 GHz (ref. 2). However, fundamental physical processes for a silicon-based optical modulator in the terahertz bandwidth range have not yet been explored. Here, we demonstrate ultrafast phononic modulation of the optical index of silicon by irradiation with intense few-cycle femtosecond pulses. The anisotropic reflectivity modulation by the resonant Raman susceptibility at the fundamental frequency of the longitudinal optical phonon of silicon (15.6 THz) generates a frequency comb up to seventh order. All-optical >100 THz frequency comb generation is realized by harnessing the coherent atomic motion of the silicon crystalline lattice at its highest mechanical frequency.

The coherent modulation of electronic and vibrational nonlinearities in atoms and molecular gases by intense few-cycle pulses has been used to generate high-harmonic optical pulses in the soft X-ray and attosecond regime, as well as Raman frequency combs that span multiple octaves from the terahertz to petahertz (infrared to vacuum ultraviolet) frequency regions. In principle, similar high-order nonlinear processes can be excited efficiently in solids and liquids because of their high nonlinear polarizability densities. In practice, however, optical absorption, phase matching and competition from other nonlinear processes (for example, white light generation) limit applications of solid-state materials to low-order electronic processes, such as second-harmonic generation and optical rectification. The nonlinear optical responses of solid surfaces, however, have been extended to high-harmonic generation and multi-photon photomission. One might therefore anticipate that coherent vibrational Raman processes in a highly nonlinear regime could also modulate light at multiple phonon frequencies in the 1–100 THz range.

The impulsive excitation of a crystalline lattice into a quantum optical coherent state corresponding to oscillation at its highest mechanical frequency, the zone-centre longitudinal optical (LO) phonon (coherent phonon), has been used to study nonlinear light–matter interactions, as well as electron–phonon and phonon–phonon coupling. Coherent LO phonon spectroscopy and dynamics have been studied for insulators (diamond), semiconductors (GaAs and silicon) and semimetals (bismuth and graphite), metals and ferroelectrics and organic crystals. In many materials, including silicon, the sudden generation of dense electron–hole plasma both drives the coherent lattice vibration and induces lattice softening, potentially causing a structural phase transition. The novel environment of such non-equilibrium plasmas could also promote highly nonlinear light–matter interactions that are absent in transparent materials.

Here, we explore the coherent phonon-induced refractive index modulation of a Si(001) surface upon excitation at ≈397 nm (3.12 eV) in near-resonance with the direct bandgap of silicon (≈3.4 eV) (Fig. 1). By means of anisotropic electron–hole pair generation and coherent Raman scattering, laser pulses with an energy of <1 mJ and duration of ~10 fs exert a sudden electrostrictive force on the silicon lattice, launching coherent LO phonon oscillations at a frequency of 15.6 THz. With more than one order of magnitude larger amplitude than for non-resonant impulsive simulated Raman excitation, the LO phonon oscillation strongly modulates the direct bandgap of silicon through the optical deformation potential. The concomitant oscillatory change in the optical constants modulates the reflected probe light at the fundamental LO phonon frequency, generating a broad comb of frequencies at exact integer multiples of the fundamental frequency and extending to beyond 100 THz. On the basis of an analytical model, we show that the simultaneous amplitude and phase modulation of the reflected light by the coherent lattice polarization at 15.6 THz generates the frequency comb.

Figure 2 shows the transient electro-optic reflectivity of the Si(001) sample upon excitation by a pump pulse with a fluence of 1 mJ cm−2, which is measured by scanning the pump–probe delay and recording the intensity difference between the orthogonal polarization components of the reflected light. Following an initial periodic electronic response, which follows the onset of the electrostrictive force, the signal oscillates with a period of ~64 fs of the zone-centre coherent LO phonon and decays within several picoseconds. The coherent LO phonon response in Fig. 2 can be approximately simulated as a damped oscillator with amplitude A, frequency ωLO, and chirp η, delay-dependent relaxation time (τLO + vt) and initial phase φ.

\[
\frac{\Delta R_{EO}(t)}{R_0} = A \exp\left[-t/(\tau_{LO} + vt)\right] \cos\left(\omega_{LO}t + \eta t + \phi\right)
\]

The LO phonon frequency, relaxation time and phase depend on the photoexcited carrier density, which varies with both pump fluence and delay. The frequency shift and relaxation time change are manifestations of the complex self-energy for LO phonon
interaction with photoexcited carriers (Table 1). The self-energy depends on the delay time as the carriers in the probing region relax to a thermal distribution and decay through transport. The new finding from our experiment is evident in the residual of the fit in the inset to Fig. 2; in addition to the dynamics represented by equation (1), the electro-optic response oscillates at the second and higher-order harmonics of the LO frequency with periods of 32, 21, 16 fs, and so on, down to 9 fs.

To further characterize the phonon-induced light modulation, Figure 3a presents the power spectrum of the transient reflectivity response by obtaining the Fourier transform of the time-domain signal in Fig. 2. The Fourier transform spectrum reveals that the modulated signal consists of an evenly spaced comb of frequencies dominated by the fundamental LO phonon oscillation at 15.6 THz, followed by a progression of its exact harmonics. The evenly spaced Fourier transform line spectrum is reminiscent of a Raman frequency comb that can be generated through cascaded nonlinear interactions in the transmission of intense laser pulses through transparent media. In the case of the absorbing silicon surface, however, the reflection depth and time are much less than an optical cycle, so causally related multiple scattering through a cascading process cannot occur. Moreover, the frequency comb cannot be attributed to phonon ladder climbing or Raman overtone scattering, because these processes would produce anharmonic progressions. Therefore, we seek an explanation in the complex Raman polarization induced by the resonant pump pulse.

Our observation of the frequency comb is consistent with excitation of terahertz Raman polarization, which modulates the optical constants of silicon through the optical deformation potential interaction. The electric field components \( E_k \) and \( E_l \) of the pump pulse in near-resonance with the direct bandgap of silicon exert a longitudinal force on the silicon sample by means of a combination of charge density fluctuation and coherent Raman processes. The external field acts on the sample through the second-order nonlinear susceptibility \( \chi^{(2)}(\omega_{\text{LO}},\omega_{\text{LO}}-\omega) \) to generate a rectified, longitudinal polarization, \( P_{\text{LO}}(t) = \chi^{(2)} \cdot E_k(t)E_l(t) \), which is dominated by the coherent LO phonon response. Through the electro-optic effect, \( P_{\text{LO}}(t) \) modulates with
the opposite phase the \( E_\text{p} \) and \( E_\text{i} \) components of the reflected probe light, generating collinear Stokes and anti-Stokes sidebands, \( \omega_{\pm} \), via the nonlinear electro-optic Raman susceptibility, \( \chi_{\text{EO}}^{(2)}(\omega_1; \omega_0 \pm \omega_{\pm}) \) (Fig. 1b).

To explain the observed frequency comb generation, we model the electro-optic response by calculating the effect of \( \mathcal{E}_\text{t}(t) \) on the incident field \( E_\text{p} \cos(\omega_0t) \) of the probe. In response to \( P_\text{p}(t) \), the longitudinal component of the reflected probe electric field \( E_{\text{p}}(t) \) has experienced a phase and amplitude modulation,

\[
E_{\text{p}}(t) = \left[ a(t) \cos(\omega_0 t) + R_0 \right] E_\text{p} \cos(\omega_0 t - \delta(t) \cos(\omega_0 t + \varphi))
\]

where \( a(t) \cos(\omega_0 t) \approx \chi_{\text{EO}}^{(2)} \cdot I \) describes the amplitude modulation and \( \delta(t) \cos(\omega_0 t + \varphi) \approx \chi_{\text{EO}}^{(2)} \cdot J \) the phase modulation, with a pump intensity \( I = |E_\text{p}|^2 \), \( a(t) = a_0 e^{-t/\tau_0} \) and \( \delta(t) = \delta_0 e^{-t/\tau_0} \). Other parameters are the static reflectivity \( R_0 \), the optical carrier frequency \( \omega_0 \), and the relative phase between the amplitude and phase modulation, \( \varphi \). The physical mechanism for the change in the real \( (n) \) and imaginary \( (k) \) parts of the index of refraction is the bandgap renormalization, that is, the energy shift (\( \Delta \varepsilon \)) of the band edge by the optical deformation potential \( \Xi \) (Fig. 1c), which is defined by \( \Delta \varepsilon = \Xi |\Delta Q|/Q_0 \) (ref. 26), where \( \Delta Q \) is the internal displacement (Si–Si) due to the optical phonon and \( Q_0 \) is the static value of the Si–Si bond length. The \( |\Delta Q| \) dependence of the bandgap and therefore the optical constants is expected for the \( \Gamma_{25} \) symmetry vibration of a crystal with an inversion symmetry.

The Fourier transform spectra of the simulated time-domain electro-optic response of silicon based on equation (2) are presented in Fig. 3b. Together, the amplitude and phase modulation of the reflected probe light reproduce the frequency comb, consistent with the experiments. Specifically, the simulation reproduces (i) the evenly spaced frequencies forming the comb at multiples of the exact LO phonon frequency, (ii) line broadening as the order number increases, (iii) the even–odd-order intensity alternation, and (iv) the alternating asymmetric lineshapes of the higher orders. The asymmetry is best reproduced with a relative phase of \( \varphi \approx 0 \) between the amplitude and phase modulation. Simulating the reflected field with phase modulation only \( (a_0 = 0; \text{Fig. 3b}) \) generates even orders only, whereas amplitude modulation \( (\delta_0 = 0) \) only generates the fundamental and second orders. The simulations therefore show that the frequency comb arises from the combined action of amplitude and phase modulation of the probe light.

An additional manifestation of bandgap renormalization is the dependence of the coherent phonon phase \( \phi \) on excitation density (Table 1). At low densities, the coherent phonon phase \( \phi \) is close to the impulsive limit \( (\phi \approx 90^\circ) \), indicating that the applied force is dominated by the Raman susceptibility59. In contrast, at high densities, bandgap renormalization during excitation brings the direct bandgap of silicon into resonance with the excitation light, so that the anisotropic excitation of L-valley carriers exerts a displace electrostrictive force \( (\phi = 0^\circ) \)14,17,20. We note that when replacing the amplitude and phase modulation by sine functions in equation (2), as appropriate for the impulsive limit, the simulation reproduces the Fourier transform spectra obtained with 30 mW excitation, corresponding to a lower photoexcited carrier density \( (N \approx 0.5 \times 10^{20} \text{ cm}^{-3}) \).

In summary, we have discovered a new approach for ultrafast light modulation by coherent phonon excitation. Terahertz polarization at the zone-centre LO phonon frequency (15.6 THz) of silicon acts via the complex Raman susceptibility on the phase and amplitude of the reflected light. The resulting frequency comb that is impressed on the reflected light extends up to the seventh order (109.2 THz) of the highest mechanical frequency of

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**Table 1 | Parameters obtained by the fit of the transient electro-optic response at various pump fluences.**

| Pump fluence (mJ cm\(^{-2}\)) | Frequency (THz) | Relaxation time (ps) | Chirp (ps\(^{-2}\)) | Initial phase (deg) |
|-----------------------------|----------------|----------------------|------------------|-------------------|
| 0.08                        | 15.613         | 3.62                 | 0.00381          | 68.0              |
| 0.50                        | 15.596         | 2.12                 | 0.00629          | 60.7              |
| 1.00                        | 15.587         | 1.31                 | 0.01120          | 10.0              |
the driving polarization and is limited in bandwidth by the duration of the probe pulse. The characteristic spectral features of the frequency comb can be attributed to the simultaneous action of the amplitude and phase modulation on the electric field of the probe light during the process of reflection from the silicon surface. The strong nonlinear interaction that creates the effective anisotropic reflectivity. The strong nonlinear interaction that creates the effective anisotropic reflectivity.

**Figure 3 | Fourier transform spectrum obtained from the transient anisotropic reflectivity.** a, Fourier transform spectrum of the reflectivity signal of Fig. 2. Inset: width of the higher-order terms as a function of their order \( \beta \). b, Fourier transform spectra of the reflectivity signal calculated using the model in equations (2) to (4). Spectra are simulated with the amplitude and phase modulation (with \( \varphi \approx 0 \) in equation (2)) acting together or separately. The experimental frequency comb generation can only be reproduced by including both phase and amplitude modulation, as described in the main text.

**Methods**

**Ultrafast spectroscopy.** The anisotropic transient reflectivity of an n-doped (1.0 \( \times 10^{18} \) cm \(^{-3} \)) Si(001) wafer was measured in air at 295 K using the electro-optic sampling technique. Nearly collinear pump and probe beams (397 nm (3.12 eV) central wavelength) were overlapped at a 7.2 \( \times 10^{-7} \) cm\(^2\) spot on the sample. The frequency-doubled Ti:sapphire laser oscillator with an average power of 60 mW and a 70 MHz repetition rate generated \( N \approx 1.0 \times 10^{20} \) cm\(^{-3} \) carriers, as estimated from the absorption coefficient \( \alpha = 1.2 \times 10^7 \) cm\(^{-1}\) at 397 nm (ref. 30). This carrier density is one to two orders of magnitude less than the thresholds for optical damage and optically induced melting of silicon. The polarization of the pump beam was set to the [110] direction, and that of the probe to [100]. The reflected probe beam was analysed into polarization components parallel and perpendicular to that of the pump and each was detected with a photodiode. The resulting photocurrents were subtracted and after amplification their difference \( \Delta R_1/\Delta R_2 = (\Delta R_1 - \Delta R_2)/\Delta R_1 = (|E_1|^2 - |E_2|^2)/|E_1|^2 \) was recorded versus the pump–probe delay. The delay was scanned over 10 ps and averaged for 20,000 scans by using an oscillating retroreflector with a 20 Hz scan frequency.

**Numerical simulation.** Generation of the frequency comb was simulated by calculating the modulation of the probe light through the complex Raman susceptibility by coherent LO phonon oscillation (Fig. 1a,b). The terahertz Raman polarization modulates the complex index of refraction \( n = n + i \kappa \). In silicon at 3.12 eV, the real and imaginary parts are \( n = 5.57 \) and \( \kappa = 0.387 \), so \( n > \kappa > \kappa \) (ref. 30). The derivatives of \( n \) and \( \kappa \) with respect to photon energy (\( h\omega \)) are, however, different, with \( d\kappa/d\omega \) being larger than \( dn/d\omega \) near the bandgap. Consequently, \( \Delta n \gg \Delta \kappa \) does not hold, and both \( \Delta n \) and \( \Delta \kappa \) contribute to the light modulation. In equation (2) we define \( \delta_0 = (2\pi\lambda_0 \Delta n)/\lambda_0 \approx 1.30\lambda_0 \), where \( \Delta \kappa = \Delta n = \Delta |Q_x| \) (refs 26, 27), \( \lambda_0 = 60 \mu\)m and a 70 MHz repetition rate generated \( N \approx 1.0 \times 10^{20} \) cm\(^{-3} \), so \( \Delta \kappa = d\kappa/d\omega \approx 1.80 \mu\)m. Furthermore, from the Fresnel's coefficient with nearly surface normal incidence, \( \alpha = 2\pi\kappa/(n + 1) = 2.046\lambda_0 \) if \( \Delta \kappa > \Delta n \), where \( \Delta \kappa \approx \Delta n \approx \Delta |Q_x| \). The ratio of the magnitudes of the phases and amplitude modulations used in the simulation thus becomes \( \delta_0/\alpha \approx 28 \). Using the Jacobi–Anger identity, we can expand equation (2) as

\[
\cos[\delta(t)\cos(\omega_0 t + \varphi)] = J_0(\delta(t)) - 2J_2(\delta(t))\cos(2\omega_0 t + 2\varphi) + 2J_4(\delta(t))\cos(4\omega_0 t + 4\varphi) - \cdots
\]

\[
\sin[\delta(t)\cos(\omega_0 t + \varphi)] = J_1(\delta(t))\cos(\omega_0 t + \varphi) - 2J_3(\delta(t))\cos(3\omega_0 t + 3\varphi) + 2J_5(\delta(t))\cos(5\omega_0 t + 5\varphi) - \cdots
\]

where \( J_0(z) \) is the Bessel function of the first kind of order \( i = 0, 1, 2, \ldots \). Using these relations, equation (2) can be rewritten as

\[
|E_p(t)|^2/E_0^2 \approx 2a_0 R_0 \left[ J_0^2(\delta(t)) + \frac{a_0}{2} J_2^2(\delta(t)) + \frac{a_0}{2} J_4^2(\delta(t)) + \frac{a_0}{2} J_6^2(\delta(t)) + \frac{a_0}{2} J_8^2(\delta(t)) \right] \cos(\omega_0 t)
\]

\[
+ 2 a_0 R_0 \left[ \frac{1}{4} J_0^2(\delta(t)) - J_2(\delta(t)) - J_4(\delta(t)) - J_6(\delta(t)) + J_8(\delta(t)) \right] \cos(2\omega_0 t) + \frac{1}{4} a_0 R_0 \left[ J_0^2(\delta(t)) + J_2^2(\delta(t)) + J_4^2(\delta(t)) + J_6^2(\delta(t)) \right] \cos(4\omega_0 t)
\]

\[
+ 2 a_0 R_0 \left[ \frac{1}{8} J_0^2(\delta(t)) - J_2(\delta(t)) + J_4(\delta(t)) \right] \cos(6\omega_0 t) + \cdots
\]

In equations (3) and (4), we neglect terms higher than the fifth order \( J_2, J_4, \ldots \) because of their \( 10^{-2} \) to \( 10^{-3} \) smaller values than the lower orders. Including the fifth- and sixth-order terms in equations (3) and (4) generates responses up to the
12th order of the LO phonon frequency (~200 THz), which is beyond the bandwidth of our laser. In equation (4) we note that the amplitude for the odd–even order terms (except the second order) do not; this difference explains the odd–even order intensity alternation. Furthermore, for pure amplitude modulation (that is, when $\delta_0 = 0$), then $I_q = 1$ and $I_{j} (i = 1, 2, 3\ldots) = 0$, and only the first and second orders appear (see Fig. 3b), because only these orders include the $L_q$ term in equation (4). Finally, we note that a simple argument with amplitude modulation being expressed by $E_{in} = E_0 \Delta \varepsilon \propto |\Delta Q| \approx |\cos(\alpha_{Q,LO})|$ and phase modulation by $E_{in}(t) = E_0 \cos(\Delta \varphi) \approx E_0 \cos[\cos(\alpha_{Q,LO})] \approx E_0 [1 - 1/2 \cos^2(\alpha_{Q,LO}) + \ldots]$ gives the same qualitative behaviour as the calculated amplitude and phase modulation contributions from the solution of the Bessel equations (Fourier transform spectra in Fig. 3b).

Received 22 August 2011; accepted 30 January 2012; published online 4 March 2012

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Acknowledgements

The authors acknowledge M. Kitajima for stimulating discussions. This work was supported in part by the National Science Foundation (grant no. CHE-0650756).

Author contributions

M.H. and A.M.C. performed the experiments and analysed data. M.K. constructed the simulation model and M.H. carried out the model simulation. M.H., M.K. and H.P. discussed the results. M.H. and A.M.C. performed the experiments and analysed data. M.K. constructed the simulation model and M.H. carried out the model simulation. M.H., M.K. and H.P. discussed the results. M.H. and H.P. co-wrote the manuscript.

Additional information

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