Four-wave mixing experiments with extreme ultraviolet transient gratings

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Four-wave mixing (FWM) processes, based on third-order nonlinear light–matter interactions, can combine ultrafast time resolution with energy and wavevector selectivity, and enable the exploration of dynamics inaccessible by linear methods1–7. The coherent and multiwave nature of the FWM approach has been crucial in the development of advanced technologies, such as silicon photonics8, subwavelength imaging9 and quantum communications10,11. All these technologies operate at optical wavelengths, which limits the spatial resolution and does not allow the probing of excitations with energy in the electronvolts range. Extension to shorter wavelengths—that is, the extreme ultraviolet and soft-X-ray ranges—would allow the spatial resolution to be improved and the excitation energy range to be expanded, as well as enabling elemental selectivity to be achieved by exploiting core resonances4–7,11–14. So far, FWM applications at such wavelengths have been prevented by the absence of coherent sources of sufficient brightness and of suitable experimental set-ups. Here we show how transient gratings, generated by the interference of coherent extreme-ultraviolet pulses delivered by the FERMI free-electron laser15, can be used to stimulate FWM processes at suboptical wavelengths. Furthermore, we have demonstrated the possibility of observing the time evolution of the FWM signal, which shows the dynamics of coherent excitations as molecular vibrations. This result opens the way to FWM with nanometre spatial resolution and elemental selectivity, which, for example, would enable the investigation of charge-transfer dynamics16–19. The theoretical possibility of realizing these applications has already stimulated ongoing developments of free-electron lasers16–20; our results show that FWM at suboptical wavelengths is feasible, and we hope that they will enable advances in present and future photon sources.

In FWM, three coherent fields interact within the sample via the third-order susceptibility $\chi^{(3)}$, which, unlike the second-order susceptibility, does not vanish by reason of the sample symmetry1,2; FWM processes thus represent the lowest-order (non-vanishing) optical nonlinearity for most materials. The FWM concept is the basis of many coherent nonlinear methods, such as coherent Raman scattering, multi-dimensional spectroscopy, and impulsive stimulated Rayleigh, Brillouin and Raman scattering1–7,11. These applications are based on dynamic (transient) gratings, generated by periodic modulations of the sample’s optical properties by different excitations that ultimately drive the time evolution of the created gratings. Hence the capability to generate, control and probe the time dependence of extreme-ultraviolet (EUV) transient gratings at ultrafast timescales is an essential step towards the development of FWM at suboptical wavelengths. Though the potential high impact of using short-wavelength photons has been discussed in a number of theoretical and perspective works8–10,12,21 and evidence for basic EUV/X-ray nonlinear processes has been reported22–23, the experimental investigation of FWM in this spectral range has been prevented by the lack of fully coherent sources with high brilliance. In this Letter we report experimental evidence of FWM processes stimulated by EUV transient gratings, generated by two coherent EUV pulses provided by the FERMI FEL15.

Figure 1 shows a sketch of the experiment: two FEL pulses (wavelength $\lambda_{\text{EUV}} = 27.6\,\text{nm}$, estimated time duration 60–80 fs, pulse energy $I_{\text{EUV}1} = I_{\text{EUV}2} = 5\,\mu\text{J}$, spot size $\sim 0.04\,\text{mm}^2$) are crossed (angle $\Delta \theta = 6.16^\circ$) on a vitreous SiO$_2$ sample with the surface oriented orthogonally to the bisector of the FEL beams. The interference of the two pulses generates EUV transient gratings with a spatial periodicity $L = \lambda_{\text{EUV}}/2\sin(\theta) = 256.8\,\text{nm}$. An optical pulse ($\lambda_{\text{opt}} = 392.8\,\text{nm}$, time duration $\sim 100\,\text{fs}$, pulse energy $I_{\text{opt}} = 2\,\mu\text{J}$, spot size $\sim 0.002\,\text{mm}^2$), coplanar with the FEL beams, was sent into the sample at an angle of incidence $\theta_B = 49.9^\circ$. The polarization of the fields was orthogonal to the scattering plane. The chosen values of $\lambda_{\text{EUV}}$, $\lambda_{\text{opt}}$, $\theta$ and $\theta_B$ fulfil the phase matching condition (see Fig. 1b), in which the present transient grating experiment reduces to: $\lambda_{\text{EUV}}\sin(\theta_B) = \lambda_{\text{opt}}\sin(\theta)$. This determines the propagation direction of the FWM signal: $k_{\text{FWM}} = k_{\text{EUV1}} - k_{\text{EUV2}} + k_{\text{opt}}$, where $k_{\text{EUV1,2}}$ and $k_{\text{opt}}$ are the wavevectors of the EUV fields and of the optical field, respectively. Along $k_{\text{FWM}}$, the nonlinear signal, radiated by different portions of the sample, adds coherently, yielding a FWM signal propagating downstream from the sample as a well-defined beam1–7,21. The experiment was carried out at the DiProI end-station using a purposely designed experimental set-up based on reflective optics (see Methods for details). Such a set-up lets us adjust $2\theta$, $\theta_B$, the time delay between the crossed FEL pulses ($\Delta t_{\text{FEL-EUV}}$) and the delay between the FEL pulses and the optical pulse ($\Delta t$). FEL-pump/optical-probe transient reflectivity measurements were used to determine $\Delta t_{\text{FEL-EUV}} = 0$ and to equalize the fluorescence of the two FEL pulses in the...
Concerning the magnitude of the nonlinear effect, the strength of the FWM field radiated by the sample ($I_{\text{FWM}}$) is related to those of the input fields as $I_{\text{FWM}} \approx \chi^{(3)} E_{\text{EUV1}} E_{\text{EUV2}} E_{\text{opt}}$; in the present case we estimated $E_{\text{EUV1}} \approx E_{\text{EUV2}} \approx 0.8 \times 10^5 \text{ V m}^{-1}$, so that an effective value for the third-order susceptibility $\chi^{(3)}$ is $\approx (\eta_{\text{FWM}})^{1/2}$ ($E_{\text{EUV1}}, E_{\text{EUV2}} \approx 6 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$ (at $\Delta t = 0$) can be estimated. This value is within the expected order of magnitude, since $\chi^{(3)}$ scales as $E_1^{1-3}$, where $E_1 \approx e(4\pi e_0 \Delta x)^2 \approx 5 \times 10^{11} \text{ V m}^{-1}$ is the atomic field strength (here $e$, $e_0$, and $\Delta x$ are the elementary charge, the dielectric constant, and the Bohr radius, respectively).

The time evolution of $\eta_{\text{FWM}}$ is shown in Fig. 3a. The data are scaled by the factor $\eta = I_{\text{FWM}}(\Delta t = 0) I_{\text{EUV1}}(\Delta t = 0) I_{\text{EUV2}}(\Delta t = 0)$, where $I_{\text{EUV1}}(\Delta t = 0)$ and $I_{\text{EUV2}}(\Delta t = 0)$ were detected. For $\Delta t > 0$, an appreciable FWM signal is observed over the whole probed range of $\Delta t$ (that is, up to 130 ps). The signal observed at large values of $\Delta t (>10 \text{ ps})$ can be ascribed to thermal relaxation and longitudinal acoustic modes. The latter are expected to induce a signal modulation at frequency $\nu_{\text{LA}} = c_0/L \approx 23.2 \text{ GHz}$, where $c_0 = 5.970 \text{ m s}^{-1}$ is the velocity of sound in vitreous $\text{SiO}_2$, which is compatible with our data. Figure 3b displays the FWM signal in the range 0 to 1.6 ps after $R_{\text{ex}}(\Delta t)$ has been subtracted. Here the time structure of the FWM signal is compatible with two oscillations at frequencies $\nu_1 \approx 1.15 \text{ THz}$ and $\nu_2 \approx 4.1 \text{ THz}$. The latter frequency roughly matches that of the $\nu_{2\text{ph}}$ Raman modes, due to tetrahedral bending, while the former, which accounts for the leading modulation of the observed FWM signal, can be ascribed to $\nu_1$ hyper-Raman modes, which involve rotations of $\text{SiO}_4$ tetrahedra (see Methods for details).

Our results demonstrate the generation of dynamic EUV gratings using fully coherent FEL pulses. The nonlinear interactions between the induced grating and an optical pulse allow us to observe the first FEL-stimulated FWM signal, which encodes the dynamics of impulsively stimulated collective vibrational modes with wavevector $k_{\text{ex}} = |k_{\text{EUV1}} - k_{\text{EUV2}}|$ (Ref. 3). This shows how EUV transient gratings can be used to drive coherent excitations into the sample, and paves the way for the practical exploitation of nonlinear optics in the EUV/soft X-ray (SX) range. In this context, we aim to replace the optical pulse with an EUV/SXR pulse (EUV probing of optically stimulated transient gratings has already been reported$^{25,26}$) to probe vibrational modes in the range $k_{\text{ex}} = 0.1–1 \text{ nm}^{-1}$ (Ref. 21). This range, inaccessible by optical FWM (see Fig. 4a), can be probed by using photon wavelengths down to 10 nm (that is, well within the range of FERMI$^{25}$), and is of special relevance for the investigation of disordered systems. Indeed, the origin of the thermodynamic peculiarities of such systems (for example, the highly debated excess specific heat) seems to be related to ‘mesoscopic’ heterogeneities that extend over a length scale of a few nanometres, which can be revealed by the anomalous behaviour of vibrational modes in the range $k_{\text{ex}} = 0.1–1 \text{ nm}^{-1}$ (Refs 29, 30).

An opportunity offered by the FEL technology is the use of two-colour FEL pulses$^{16-17}$ to generate coherent populations of excited states expected signal modulation due to acoustic modes, respectively (right-hand y axis plots same quantity as left-hand axis, but on an expanded scale). Black circles connected by lines are the FWM signal after $R_{\text{ex}}$ is subtracted. The red line is the modulation due to oscillations at frequencies $\nu_1 = 1.15 \text{ THz}$ and $\nu_2 = 4.1 \text{ THz}$. Error bars, as a.

Figure 3: Time evolution of the FWM signal. a, Black circles (connected by lines where there is enough distance between adjacent points) show the time dependence of the FWM signal, scaled to the intensity of the input beams (error bars are estimated as one standard deviation of the set of CCD images corresponding to the same $\Delta t$ value); the blue and red lines are $R_{\text{ex}}$ and the
via FWM processes, such as coherent Raman scattering (CRS)\(^\text{2.6–7}\). In CRS, the excitation energy and wavevector are set by the difference in photon energy \((\omega_{\text{ex}} = \omega_1 - \omega_2)\) of the stimulating pulses and by the grating vector \(k_{\text{ex}} = k_1 - k_2\), respectively (see Fig. 4b and c). Compared to the optical regime, EUV/SXR pulses (10–1,000 eV) will allow us to coherently stimulate excitations at higher energy (for example, excitons with \(\omega_{\text{ex}} = 1–10\text{ eV}\))\(^\text{2.6–7}\). These can be probed by a third pulse, generated by the FEL\(^\text{3,6,20}\) or by an external source\(^\text{27,28}\). Furthermore, when the field frequencies of the stimulating and/or probing pulses are tuned to core resonances of given atoms, the localization of core shells turns into an atomic-scale localization of the site at which the selected excitation is created and/or probed (see Fig. 4c and d). So by tuning the field frequencies and time delay it is possible to use FWM to gain real-time information on the excitation transfer between selected atomic sites. This possibility is forbidden in linear inelastic scattering, where the light–matter interaction takes place at the same atomic site\(^7\).

In the future, multi-wave interactions would allow the application of a time delay (\(\tau\), see Fig. 4c) between the excitation pulses (for example, by setting \(\Delta t_{\text{EUV,EUV}} = \tau \neq 0\) in our set-up). This is a substantial step towards multi-dimensional spectroscopy\(^4\), and may enable resonant and non-resonant FWM signals to be distinguished. For experimental reasons, core-resonant FWM is still an unexplored field, though solid theoretical approaches and numerical studies in the SXR region are available\(^7,11\). Core-resonant FWM will soon be tested at FERMI, since many elements (such as C, Mg, Al, Si, Ti) have resonances within the photon energy range of this FEL (20–310 eV). The third harmonic of the FERMI FEL emission (photon energy range: 60–930 eV) and the forthcoming construction of self-seeded SXR FEL sources with a wider photon energy range (for example, SCLS-II, SwissFEL and PAL-XFEL) could most probably be used to exploit resonances at higher energy.

FWM with elemental selectivity could have applications\(^2,32\) in the study of charge transfer dynamics in electrocatalytic processes occurring in photoelectrochemical cells; these devices mimic natural photosynthesis to convert sunlight into chemical energy. Photoelectrochemical cells are typically based on molecular complexes adsorbed on TiO\(_2\) substrates, and have a conduction/valence band dominated by the TiO-orbitals. FWM with elemental selectivity may be able to disentangle the timescales of electron and hole migration, by exploration of the Ti and O resonances, and to shed light on the water oxidation dynamics taking place at the catalyst by separating the signal originating from reaction centres\(^6\). Since elements of biological interest (C, N, O) have resonances in the EUV/SXR range, applications in life sciences are also very likely.

Online Content: Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

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Author Contributions C.M. proposed and led the project to extend transient grating methods at suboptical wavelengths. F.B. conceived the experiment and coordinated all activities. F. Capotondi designed the set-up to split and recombine the FEL pulses. A.G. realized the set-up and, together with F. Capotondi, A.B. and R.M., integrated it into the end-station. F.B., R.C., F. Capotondi, A.B., R.M., E.G., M.M., E.P., E.P., M.K. and C.M. performed the experiments and analysis. F.B., R.C., A.B., A.G. and R.M. tested the set-up. I.P.N. and M.B.D. realized the set-up and, together with F. Capotondi, A.B. and R.M., integrated it into the end-station. F.B., R.C., F. Capotondi, A.B., A.G. and R.M. tested the set-up. I.P.N. and M.B.D. realized the set-up to control the optical pulse. F.B., R.C., F. Capotondi, A.B., R.M., E.G., M.M., E.P., E.P., C.S. and F. Casolini performed the experiment. A.B., R.M., F.B., R.C., F. Capotondi and M.M. carried out the data analysis. P.P., C.S., A.B. and R.M. performed the AFM measurements and analysis. F.B., R.C., F. Capotondi, A.B., M.B.D., M.K. and C.M. discussed the data. F.B. and C.M. prepared the manuscript.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to F.B. (filippo.bencivenga@elettra.eu) or C.M. (claudio.masciovecchio@elettra.eu).
METHODS

Experimental set-up. The FEL focusing was provided by a Kirkpatrick-Baez active focusing system (located upstream of the DiPro1 end-station)\(^1\), which was detuned to relax the spot size at the sample in order to avoid sample damage. The FEL photodiagnostic data were acquired on a shot-to-shot basis by the Photon Analysis, Delivery and Reduction System (PADReS)\(^2\), which connects the FEL source to the end-station; an Al filter placed along the photon transport line was used to remove the seed laser radiation.

The layout of the experimental set-up used to generate and probe EUV transient gratings is shown in Extended Data Fig. 1. The system to split and recombine the FEL beams (see Extended Data Fig. 1a) is based on three 70-mm-long carbon-coated mirrors (M1, M2 and M3) working at grazing incidence. It is mounted on a 580 mm × 280 mm baseplate and in the present case the grazing angles were ~3°. M1 can be inserted into the path of the incoming FEL beam by a y-translation (see Extended Data Fig. 1a for the adopted reference frame) and is used as a wavefront division beamsplitter.\(^2\),\(^3\),\(^4\) The two split beams propagating downstream of M1 are recombined on the sample by mirrors M2 and M3. The design position of the mirrors corresponds to a paralellogram geometry, where the splitting angle after M1 (2x) equals the crossing angle at the sample (2l) and the M1–M2 distance (d1) equals the M3–sample distance (d2). In this case the optical path difference (D) between FEL path 1 (FP1) and FEL path 2 (FP2) vanishes, ensuring the time coincidence of the two FEL beams. The design values of the system are 2x = 2l = 6° and d1 = d2 = 125 mm. The system has several motorized degrees of freedom to adjust the mirror positions and angles during the experiment: (1) the pitch and roll angles of all mirrors can be independently controlled in the ±3.5° range with a resolution of ~50 μrad by piezo-electric steering motors; (2) the y-position of M1 can be changed in the ±20 mm range with ±2 μm resolution; (3) the x and y positions of M2 and M3 can be independently varied in the ±9.5 mm range by linear piezomotors with a resolution of ~0.2 μm; (4) each mirror can be removed from the FEL paths; (5) the whole system can be adjusted in x, y and z. Furthermore, the sample is mounted on a (x, y, z, pitch, roll) adjustment stage, which also allows the SiO\(_2\) sample to be replaced with a fluorescent screen, a pinhole (PHsam) or a Si\(_3\)N\(_4\) reference sample (for cross-correlation measurements described further below). Such motors can be used to change the value of 2l (in the 3°–9° range) keeping the time difference of the two FEL pulses (Δ(l) (EUV,EUV)) or vice versa; see sketches in Extended Data Fig. 1d and e. The possibility of varying Δ(l) (EUV,EUV) (in the ±0.2 ps range for 2l ~ 6°) at fixed 2l makes our set-up de facto a compact split and delay device, with the advantage of the angular discrimination of the two FEL pulses.

The system was pre-aligned using a Ti:sapphire laser to simulate the incoming FEL beam and optimizing the second harmonic signal generated by a nonlinear crystal placed at the sample position (this signal is sensitive to the time–space coincidences of the two FEL beams (see Extended Data Fig. 1a) and is used as a wavefront division beamsplitter\(^2\),\(^3\),\(^4\). The two split beams propagating downstream of M1 are recombined on the sample by mirrors M2 and M3. The design position of the mirrors corresponds to a paralellogram geometry, where the splitting angle after M1 (2x) equals the crossing angle at the sample (2l) and the M1–M2 distance (d1) equals the M3–sample distance (d2). In this case the optical path difference (D) between FEL path 1 (FP1) and FEL path 2 (FP2) vanishes, ensuring the time coincidence of the two FEL beams. The design values of the system are 2x = 2l = 6° and d1 = d2 = 125 mm. The system has several motorized degrees of freedom to adjust the mirror positions and angles during the experiment: (1) the pitch and roll angles of all mirrors can be independently controlled in the ±3.5° range with a resolution of ~50 μrad by piezo-electric steering motors; (2) the y-position of M1 can be changed in the ±20 mm range with ±2 μm resolution; (3) the x and y positions of M2 and M3 can be independently varied in the ±9.5 mm range by linear piezomotors with a resolution of ~0.2 μm; (4) each mirror can be removed from the FEL paths; (5) the whole system can be adjusted in x, y and z. Furthermore, the sample is mounted on a (x, y, z, pitch, roll) adjustment stage, which also allows the SiO\(_2\) sample to be replaced with a fluorescent screen, a pinhole (PHsam) or a Si\(_3\)N\(_4\) reference sample (for cross-correlation measurements described further below). Such motors can be used to change the value of 2l (in the 3°–9° range) keeping the time difference of the two FEL pulses (Δ(l) (EUV,EUV)) or vice versa; see sketches in Extended Data Fig. 1d and e. The possibility of varying Δ(l) (EUV,EUV) (in the ±0.2 ps range for 2l ~ 6°) at fixed 2l makes our set-up de facto a compact split and delay device, with the advantage of the angular discrimination of the two FEL pulses.

Data analysis. For each probed Δl value we acquired 5 CCD images (exposure time: 1 min) with the FEL on and 2 with the FEL off. The FEL off images were used to remove the background due to diffuse scattering of the optical laser, mainly due to the fraction of the laser pulse transmitted through the sample, which then impinged on the wall of the experimental chamber. Such frequent and accurate determinations of the background allowed us to account for small drifts in the CCD response during the Δl-scan, which lasted several hours. After background subtraction we applied a low-pass Fourier filter in order to reduce the noise and improve the contrast. In order to convert the ADC counts, recorded by the CCD, into incoming photons we assumed a sensitivity of 8.5 photons per ADC count, which also takes into account the detector quantum efficiency. The total number of photons in the FWM beam was determined by fitting the peak in each image with a two-dimensional Gaussian function plus a flat background and then calculating the volume under the Gaussian surface. The volume corresponding to each image was then averaged taking into account the normalization to the corresponding mean squared FEL intensity; error bars were estimated as one standard deviation of the set of CCD images corresponding to the same Δl value (in a few cases we have a single image and we hence set the error bar equal to zero). At negative time delays (Δl < 0) and within the signal-to-noise of the employed CCD detector, the ‘FEL on – FEL off’ images can be fitted only by the background (see also Extended Data Fig. 3). Before subtraction, the Δl = 0 signal at small mirror positions and angles. The intensity stability of the FEL was typically better than 7% during the acquisition of the 5 FEL on images and about 20% throughout the whole Δl-scan. A few images were discarded due to occasional machine faults occurring during the acquisitions.

FEL-induced transient optical reflectivity changes (AR/R) from a Si\(_3\)N\(_4\) reference sample. In such measurements we first removed M3 from FP2 to collect the cross-correlation trace between the optical pulse and the FEL pulse coming from FP1. The half drop of the AR/R profile was assumed as Δl = 0. Afterwards we removed M2 and inserted M3 in order to collect the cross-correlation trace associated with the FEL pulse coming from FP2. Iterative measurements, carried out by varying the pitch of M1 and re-translating M3 keeping fixed the FEL trajectory downstream of M3 (see Extended Data Fig. 1e), allowed us to set the condition Δ(l) (EUV,EUV) = 0. In turn, the change of the amplitude of the ΔR/R drop with respect to the FEL fluence at the sample\(^2\),\(^3\),\(^4\), such measurements also allowed us to equalize the fluence level of the two FEL beams in the interaction region. Extended Data Fig. 1f and g reports typical ΔR/R traces collected out of (or in) time coincidence and without (or with) similar fluence levels in the interaction region. Once we had set the time-space coincidence of the three beams, we adjusted 2l to optimize the phase matching conditions necessary to observe the FWM signal. The latter was recorded by a Princeton Instrument PI-MTE back illuminated Charge Coupled Device (CCD) camera with frame format 2048 × 2048 pixels and 13.5 × 13.5 μm\(^2\) pixel size. The detector was positioned ~250 mm downstream of the sample and oriented at an angle of ~49°. A 15 × 5 mm\(^2\) slit was placed in front of the CCD in order to reduce spurious light, which was mainly coming from diffuse scattering of the optical pulse (transmitted through the sample) that impinged on the wall of the experimental chamber.

AFM measurements on permanent gratings. Extended Data Fig. 2a–c shows atomic force microscopy (AFM) topographies of a 8 × 8 μm\(^2\) sample area not irradiated by the FEL pulses, irradiated by ~300 shots at a fluence larger than 50 mJ cm\(^{-2}\) and, continuously irradiated by FEL pulses at low fluence, respectively. AFM scans have been performed with aXE-100 (Park Instruments) instrument, in contact mode using commercial cantilevers (Mikromasch, CSC38, spring constant k = 0.03–0.05 N m\(^{-1}\)). The output data was sampled at 1024 pixels in both directions. Extended Data Fig. 2d–f report the corresponding depth profiles of the sample surface. The non-irradiated sample shows a roughness of about 0.6 nm root-mean-square and 5 nm peak-to-valley. A grating with a peak-to-valley amplitude of about 18 nm and a period of 256.7 ± 0.9 nm (corresponding to 2l = 6.16 ± 0.02°) is clearly visible in the sample surface irradiated at high FEL fluence. The high grating visibility after multi-shot illumination indicates that the shot-by-shot fluctuations in the optical path difference (that is, in the relative phase) between the crossed FEL pulses are lower than ΔEUV,UV. Such a low phase jitter might in principle allow for lithographic applications. Indeed, the interference between coherent FEL pulses would permit permanent gratings to be imprinted with a pitch as short as a few nanometres by exploiting larger crossing angles and shorter FEL wavelengths. Extended Data Fig. 2g–i show the power spectral densities (PSD) of the data reported in Fig. 2d–f. No specific frequencies are found in the non-irradiated sample (the peak at ~35 μm\(^{-1}\) is an artefact due to the electronic noise of the employed AFM device), while the first peak at ~0.5 μm\(^{-1}\) in the PSD, shown in Extended Data Fig. 2h, reveals a modulation with a period of ~2 μm, most probably due to diffraction effects from the mirrors. The sample surface irradiated at low fluence shows a roughness similar to that of the non-irradiated sample, and frequencies ascribable to the formation of permanent gratings are absent.

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In a proof-of-principle, we assumed that the time dependence of the FWM signal is due to impulsively stimulated vibrational modes, which can be observed in the time-dependent intensity of the normalized FWM signal $I_{\text{FWM}}(\Delta t)/I_{\text{opt}}$, where $I_{\text{opt}}$ and $I$ are the intensity of the incoming optical beam and the normalizing factor quoted in the main text, respectively. We can write the following function:

$$
\frac{I_{\text{FWM}}(\Delta t)}{I_{\text{opt}}} = R(\Delta t) \otimes [A_0 \delta(\Delta t) + \sum A_i e^{-\Delta t/\tau_i} \sin(2\pi v_i \Delta t)]^2
$$

where $A_0$ and $A_i$ are scaling factors, $\otimes$ is the convolution operator, $R(\Delta t)$ is the instrumental response function, while $v_i$ and $\tau_i$ are the frequencies and damping times of the impulsively excited vibrational modes, respectively. Since an independent determination of $R(\Delta t)$ is not available, it was assumed to be a Gaussian function of unit area with a full-width at half-maximum of $135 \text{ fs}$, which is equal to that of the $\Delta t = 0$ peak in the FWM signal ($R_c(\Delta t)$; see Fig. 3a). Hence, the $A_0 \delta(\Delta t)$ term accounts for processes occurring at timescales substantially shorter than $100 \text{ fs}$.

The $e^{-\Delta t/\tau_i} \sin(2\pi v_i \Delta t)$ terms describe the time evolution of the impulsively excited vibrational modes. Considering that the excitible modes are those having vibrational periods ($v_i^{-1}$) longer than the time duration of the stimulating FEL pulses ($60-80 \text{ fs}$), the observed FWM signal could be related to: (1) acoustic modes ($v_{LA} \approx 23.2 \text{ GHz}$, where $c_s = 5.970 \text{ m/s}$ and $L = 258.8 \text{ nm}$ are the sound velocity and the transient grating pitch, respectively); (2) Raman modes within the broad band ($3-14 \text{ THz}$) associated with tetrahedral bendings and (3) $F_{2}$ modes ($\sim 1 \text{ THz}$) involving coupled rotations of $\text{SiO}_{4}$ tetrahedra. Starting from such trial frequencies, we used equation (1) to optimize the parameters that better describe the time structure of the FWM signal, once the $A_0 \delta(\Delta t)$ term was subtracted. The coarse sampling and the limited $\Delta t$-range prevented the direct determination of acoustic parameters, which were fixed to the expected values, that is, $v_{LA} = 23.2 \text{ GHz}$ and $\tau_{LA} > 1 \text{ ns}$ (we note that in the probed $\Delta t$-range $e^{-\Delta t/\tau_i} \approx 1$), while $A_{LA}$ was fixed to $1 \times 10^{-4}$ in order to fit in the observed magnitude of the FWM signal at $\Delta t > 2 \text{ ps}$. The optimized values of the other parameters are $A_i/A_{LA} = 1.4 \pm 0.2$, $v_1 = 1.15 \pm 0.15 \text{ THz}$, $\tau_1 = 5 \pm 2 \text{ ps}$, $A_2/A_{LA} = 1.4 \pm 0.2$, $v_2 = 4.1 \pm 0.8 \text{ THz}$ and $\tau_2 = 0.15 \pm 0.06 \text{ ps}$. The value of $v_1$ roughly matches the characteristic frequency of $F_1$ modes, while $v_2$ is located on the low frequency side of the aforementioned broad Raman band, which corresponds to (highly damped) $v_{3b}$, bending modes.

Finally note that a slightly worse fit (but still satisfactory) is achieved without the $A_2$ term, while the addition of other high frequency terms (such as the $v_{4b,4c}$ bendings) does not significantly improve the fitting results.

**Sample size.** No statistical methods were used to predetermine sample size.

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Extended Data Figure 1 | Experimental set-up for FEL-based FWM measurements. a, Top-view layout of the experimental set-up used to split and recombine the FEL beams. b, Top-view layout of the experimental set-up used to control the optical beam. c, Top-view picture of the set-up: the two FEL paths (FP1 and FP2) downstream of M1 and the trajectory of the optical pulse are indicated. d, Sketch of the movements needed to change $2\theta$ keeping $D_{\text{EUV-EUV}}$ fixed. e, Sketch of the movements needed to change $D_{\text{EUV-EUV}}$ keeping $2\theta$ fixed. See Methods for details of a–e. f, g, Optical reflectivity changes in Si$_3$N$_4$ induced by the FEL beam propagating through FP1 (green dots) and FP2 (magenta dots). In f, the mirrors were displaced with respect to the nominal position; a poor time coincidence and a different fluence level in the interaction region can be seen. g, Same measurements as in f after optimization of the geometry; the superposition of the two traces indicates a large improvement in the time coincidence and a similar FEL fluence in the interaction region.
Extended Data Figure 2 | AFM topographies. AFM topographies of 8 × 8 μm² areas of the sample surface as follows: in a region that was not irradiated (a), in an area irradiated by ∼300 FEL shots at a fluence larger than 50 mJ cm⁻² (b), and in an area continuously irradiated by FEL pulses at low fluence (c). d–f, Representative depth profiles of the sample surface along the green lines shown in a–c, respectively. The power spectral densities (PSD) corresponding to data reported in d–f are shown in g–i, respectively.
**Extended Data Figure 3 | Time sequence of acquired data.** Black open and crossed circles connected by lines are data shown in Fig. 3; crossed circles correspond to a scan made several hours after the one corresponding to data shown as open circles; in both scans the time delay was continuously increased. Green dots are data collected before these two scans; here we had not yet optimized the FWM signal at $\Delta t = 0$ (these data are scaled by a factor to fit the peak intensity of the data shown as black circles). Blue and red lines are the same as shown in Fig. 3.