Title
- Ultrafast Optical Generation of Coherent Bright and Dark Surface Phonon Polaritons in Nanowires
- Ultrafast Surface Phonon Polaritons in Nanowires

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Abstract
The coherence of polaritons plays a fundamental role in numerous recent experimental observations, from strong coupling to Bose-Einstein condensation, but accessing the coherence of polaritons is a difficult task due to the high energy of plasmons and excitons. However, surface phonon polaritons offer similar promises at much lower energy. Here, we demonstrate the possibility to use visible ultrafast lasers to generate and time resolve coherent surface phonon polaritons in nanowires. We show that these modes are generated through the ultrafast screening of the surface depletion field. By comparing experiments and FDTD simulations, we show that this method allows the simultaneous generation of dark and bright mode. Our observations open the way to deeper investigations of the role of coherence in the rich polariton physics.

MAIN TEXT

Introduction
The concept of coherence, which characterizes the correlation between physical properties in one system or between systems, finds applications in a wide variety of fields from medical imaging, where techniques like optical coherence tomography [1] and coherent anti-Stokes Raman scattering [2] take advantage of the coherence of light, to atomic physics with phenomena such as Bose-Einstein condensation [3, 4] or strong and ultrastrong coupling. [5, 6] To investigate the physics of the latter examples, special conditions need to be met, such as long coherence lifetime and/or strong coupling. In light-matter interactions, the coupling between light and a quasi-particle can be enhanced through the confinement of the light field in deep sub-wavelength structures. [7] Sub-wavelength confinement can be achieved using polaritons, quasi-particles resulting from the strong coupling of electromagnetic fields to electric dipoles, such as excitons or plasmons. [8, 9] The rise of polaritons have offered a new platform to investigate coherent effects, such as the realization of macroscopic quantum state, in conditions that are inaccessible to atomic gas. [10–12] However, polaritons like excitons and, in a lesser extent, plasmons occur at high frequency, which makes it difficult with current technology.
to temporally resolve their phase, i.e. their coherence, and the associated dynamics in such systems (decoherence, energy transfer...).

Coupling lower frequency photons to excitation in a material could permit the retrieval of the phase of polaritons and to follow the dynamic of coherence. This can be achieved by coupling photons to phonons in polar materials, resulting in the formation of surface phonons polaritons (SPhPs). In recent years, SPhPs have been widely studied for the numerous prospects they offer, from radiative heat transfer [13, 14] to ultra-confinement of light at THz frequencies. [15, 16] SPhPs have numerous properties that could have tremendous impact. For instance, they allow deep sub-wavelength confinement like plasmons, but the Q factor of phonons is much larger, which permits sensing with extreme precision, [17] but also to achieve large Purcell factor. [18] Another exciting perspective of SPhPs has been recently demonstrated: the strong coupling between localized and propagating SPhPs in a nanowire array. [19] Such a system allows coherent energy transfer from electromagnetic waves to localized SPhPs to propagating SPhPs and could play an important role for coherent circuit and quantum information manipulation. In order to fully grasp the potential of SPhPs for such purpose, it is important to achieve the generation and time resolved detection of coherent SPhPs.

In this letter, we study the generation and time resolved detection of SPhPs in InP nanowires using femtosecond pump-probe spectroscopy. We first propose an experimental scheme that, taking advantage of surface band bending, allow the generation and the detection of coherent SPhPs through ultrafast screening of this surface field. We then verify experimentally this mechanism by studying nanowires with different doping concentration. Then, we combine finite difference time domain simulations and experiments with nanowires embedded in different environment and we confirm that the excited vibrations are coherent SPhPs. Interestingly, we find that with this approach, we can simultaneously generate bright and dark SPhPs. Our experimental approach will enable the study of the dynamics of numerous physical processes involving SPhPs, from radiative heat transfer [13] to strong coupling. [19, 20] In addition, accessing information on the temporal coherence of SPhPs could also shed new light on the rich physics of polaritons. [6, 21, 22]

Results

Theoretical principle

Usually, SPhPs are generated through the illumination of nanostructures with light in the THz and/or far infrared frequency range. [15, 19, 23]. These steady state approaches do not allow the retrieval of the dynamic of SPhPs. To do so, we need to use pulses of light which are much shorter than the period of the SPhPs, such as femtosecond pulses of visible light. The issue to overcome here is that such pulses have energy much larger than SPhPs and it is not straightforward to couple them to SPhPs. However, through nonlinear effects or by using charges as an intermediate, it is possible to create and detect polarizations at THz frequencies using visible light.

When a visible femtosecond pulse is incident on a material, coherent vibrations at THz frequencies are generated through multiple mechanisms. The principal ones are impulsive stimulated Raman scattering (ISRS) [24], displacive excitation of coherent phonons
(DECP) [25] and transient depletion field screening (TDFS). [26, 27] ISRS and DECP can be modeled as second order optical processes. [28] In the presence of a surface field, for instance due to Fermi level pinning at the surface, third order processes, i.e. ISRS or DECP involving the surface field can take place. In addition, the generation of photocarriers can lead to a current that screens this surface depletion field and kickstarts collective ionic motion, this mechanism is known as TDFS (Fig. 1a). Considering all these effects, the coherent phonon amplitude is thus (details of the generation, including the influence of polarization and crystal can be found in the supplementary information):

\[ Q(t) \propto -\frac{e^*}{\varepsilon_0\varepsilon_\infty}\left(\chi^{(2)}I_{pump} + \chi^{(3)}I_{pump}E_s + \int_{-\infty}^{t} J(t') dt'\right) \]

With nonlinear effects, the modes that can be generated are given by the tensors \(\chi^{(2)}\) and \(\chi^{(3)}\). On the other hand, TDFS only permits the generation of polar modes. Using TDFS, LO phonons in GaAs could be investigated, [26] and should lead also to the generation of SPhPs in nanowires.

For the detection of coherent vibrations, nonlinear effects also play a fundamental role. Assuming the presence of coherent vibrations within the sample, an incoming femtosecond pulse will experience a scattering process with the vibration, resulting in a pulse with frequency at the sum of the original probe pulse frequency and the vibration’s frequency. As was the case for the generation, the scattering process can involve the surface field. The probe photons that interact with the surface vibrations then interfere with the undisturbed photons to provide a heterodyne detection, which allow the retrieval of the phase of the coherent vibrations (see Supplementary information). Overall, we can write the change of reflectivity induced by a femtosecond visible pulse as:

\[ \Delta R(t) \propto Q(t)I_{probe}(\chi^{(2)} + \chi^{(3)}E_s) \]

**Generation mechanism**

To investigate the possibility to generate coherent SPhPs, InP nanowires (NWs) were grown (see Methods). We measured transient reflectivity of these nanowires with a pump and probe wavelengths of 550 and 720 nm, respectively. The signal obtained on the nanowires with a doping concentration \(N_D = 2.5 \times 10^{19} \text{ cm}^{-3}\) is displayed in the inset of Fig. 1b. To obtain the coherent oscillations (Fig. 1b), we extracted the background, which corresponds to the electronic and thermal responses of the sample using a three-exponential decay function (see Supplementary oscillations). The signal shows a complex structure with beatings, which highlight the presence of multiple frequencies. By performing the Fourier transform (Fig. 1c), we observe four frequencies located at 8.9, 9.1, 9.8 and 10.1 THz. To further study these frequencies, we also performed Raman scattering on these samples (Fig. 1c). We observed two peaks at 8.9 and 10.3 THz, which we attribute to the TO and LO phonons of InP, respectively. The peak at 8.9 THz is common to both experimental techniques. However, the pump-probe data displays three prominent peaks between the TO and LO phonons frequencies. Due to their location within the reststrahlen band, the frequency region with \(\varepsilon < 1\), we can assume that these vibrations correspond to SPhPs. [16]
We first investigate the generation and detection mechanisms responsible for the observation of these modes. To do so, we measured the transient reflectivity and extracted the amplitude of the vibrations as a function of the doping concentration. Indeed, using a Schottky model, the surface field is given by:

\[ E_s = \sqrt{\frac{2qN_D V_{bi}}{\varepsilon_0 \varepsilon_\infty}} \]

Following the amplitude of the signal as a function of the doping concentration allows to isolate the mechanisms involving the surface field from others. For instance, if the amplitude of the signal shows no dependence on the doping concentration, we can assume the generation occurs through ISRS or DECP, while if some dependence is observed, TDFS is a more likely candidate. In Fig. 2a, we show the Fourier transform of the transient reflectivity obtained on samples with different doping concentration ranging from intrinsic to \( N_D = 4.5 \times 10^{19} \) cm\(^{-3}\), and filtered for frequencies between 8 and 12 THz.

We see the amplitude of the three modes located between the TO and LO steadily increasing with the doping concentration. From this observation, we can already conclude that the surface field is involved in the observation of these modes. To more precisely isolate the exact generation and detection mechanisms, we take a closer look at the change of amplitude with doping concentration. In Fig. 2b, the amplitude of the various peaks in the Fourier transform as a function of the doping concentration are reported, as well as a linear fit of these data. From these trends, we can separate two cases. First, for the mode at 8.9 THz, which we attributed to the TO mode, we don’t observe any doping concentration dependence. This suggest that this mode is generated through second order processes for both generation and detection. On the other hand, the amplitude of the three modes located in the reststrahlen band increase linearly with doping concentration. Since the surface field is proportional to the square root of the doping concentration, we can conclude that both the generation and detection mechanism involve the surface field. The generation of these modes therefore occurs either through a third order process, or through TDFS. For the detection, the linear dependence implies that the responsible mechanism is the third order frequency mixing process involving the surface field. This detection mechanism is like the Franz-Keldysch effect. [30]

We can further separate the generation mechanism using polarization dependent experiments (Fig. S1). The mechanisms involving charge, such as TDFS, should be insensitive to the polarization of the pump. We performed experiments with different polarization of the pump, i.e. perpendicular and parallel to the nanowires and did not observe a significant change of the amplitude of the signal. We can conclude from this observation that the vibrations are generated through the TDFS mechanism. [27, 31] Similar experiments in which we varied the probe polarization (Fig. S1) show strong variations, further demonstrating that the detection occurs through a nonlinear process.

**Surface phonon polaritons**

We now focus on the nature of these vibrations. As previously mentioned, the frequencies are in the reststrahlen band, which is a first hint that the modes we are observing corresponds to SPhPs of the nanowires. Furthermore, SPhPs, like surface plasmons, are
sensitive to the dielectric function of the surrounding medium and their frequency shift as a function of its value. We thus performed experiments in which we immersed the nanowires in a solution of CH$_2$Cl$_2$. In Fig. 3, we reproduced the Fourier transform of the transient reflectivity obtained on nanowires in air and in CH$_2$Cl$_2$.

In CH$_2$Cl$_2$, we observe a shift of all the modes except the one located at 8.9 THz, which further confirms that it corresponds to the TO modes of InP and that the three modes located at 9.1, 9.8 and 10.1 THz are SPhPs. In particular, we note that the mode at 10.1 THz, which is close to the LO phonons frequency, is shifting due to the change of surrounding medium, in stark contrast with the behaviour of the LO phonons in similar experiments with Raman scattering. [32, 33] This mode can thus unambiguously be attributed to a SPhP.

We then performed FDTD simulations to further identify which modes are generated. We performed two types of simulations: in the first case, the nanowires are excited by a plane wave, which allows the observation of bright modes, while for the second simulation, a dipole is placed close to the nanowire, which also gives access to dark modes. [34] In the bottom part of Fig. 3, we see that when using a plane wave excitation, only two modes can be observed. These modes correspond to the transverse and longitudinal SPhPs (These modes are called the transverse dipole 2 and monopole modes in Ref. [35]). However, the dominant mode we observe experimentally is absent. But, when the nanowires are excited by a dipole, additional modes are generated, including the one we observe experimentally and that we attribute to the transverse dipole 1 mode (see Supplementary information for electric field distribution of these modes). Finally, when changing the refractive index of the surrounding medium to 1.3, [36] we observe a shift like the one observed experimentally, further confirming the nature of the observed signal.

Discussion

By generating coherent bright and dark SPhPs at 10 THz in 100 nm diameter nanowires, we have achieved extremely strong confinement of the electric field. In addition, dark modes exhibit longer lifetime due to the lack of radiative decay they exhibit. In our experiments, we observed a slightly longer coherence lifetime of 3 ps for the dark modes (corresponding to a Q-factor of 30), while for the two other modes, we obtained a value of 2 ps (see Supplementary information). However, due to the strong dispersion in the nanowires’ geometry, we believe these values are only lower bounds of the coherence lifetime. The combination of strong confinement and high Q-factor should enable to reach record value of the Purcell factor. Furthermore, the high Q-factor of dark modes can be used to achieve enhanced sensitivity to the dielectric function of surrounding medium.

We have demonstrated the possibility to use ultrafast lasers to generate and detect coherent surface phonon polaritons. By screening the surface depletion field of nanowires, a polarization at THz frequencies is generated and couple to the surface phonon polaritons. Comparisons with FDTD simulations reveal that both bright and dark modes can be generated. Finally, the sensitivity of these polaritons to the dielectric environment was highlighted. This experimental approach opens a vast array of perspectives for the study with visible light of coherence in the physics of surface phonon polaritons, such as radiative heat transfer, but also the broader polariton physics.
Materials and Methods

Nanowire growth:
InP nanowires (NWs) were grown in a low pressure (100 mbar) horizontal metal organic vapor phase epitaxy (MOVPE) system using hydrogen as a carrier gas and a total flow of at 6 slm. 80 nm Au aerosol particles were deposited with an aerial density of 4 m⁻² onto a (111)B oriented InP:Fe substrate to allow for vapor-liquid-solid NW growth. The InP:Fe substrate was covered by a nominally intrinsic MOVPE-grown InP buffer layer prior to aerosol deposition. Before the actual NW growth, the samples were annealed for 10 minutes at 600º C in a PH₃/H₂ atmosphere to desorb surface oxides. Then the samples were cooled down to the growth temperature of 390 C, after which growth was initiated by introducing trimethylindium and phosphine at molar fractions of \( \chi_{\text{TMIn}} = 9.5 \times 10^{-6} \) and \( \chi_{\text{PH₃}} = 6.2 \times 10^{-3} \), respectively, for 20 seconds to nucleate the NWs. After the nucleation, the NW growth was continued for 10 min while introducing different molar fractions of H₂S in the range of \( \text{H₂S} = 0 - 6.3 \times 10^{-5} \) for the runs. The growth was finished by switching off the TMIn and H₂S supply simultaneously while cooling down to 300 C in a PH₃/H₂ atmosphere.

Femtosecond pump-probe spectroscopy:
Experiments were performed using a re-generatively amplified, mode-locked Yb:KGW (Ytterbium-doped potassium gadolinium tungstate) based femtosecond laser system (Pharos, Light conversion) operating at 1030 nm and delivering pulses of 200 fs at 2 kHz repetition rate. This laser is then used to pump two non-collinearly phase-matched optical parametric amplifiers (NOPAs). A first one (Orpheus-N, Light Conversion), was used to generate pump pulses centered at 550 nm with pulse duration of 35 fs. The second NOPA (Orpheus-N, Light Conversion), generated probe pulses at 720 nm with 40 fs pulse duration that were time delayed with respect to the pump. The pump beam was chopped at the frequency of 1 kHz using a mechanical chopper. Both beams were focused on the sample and the modifications of the probe reflectivity induced by the pump were time-resolved.

FDTD simulations:
FDTD simulations were performed using the software Lumerical. Two types of simulation were conducted. For both simulations, we used a 110 nm diameter and 1500 nm length InP nanowire on an InP substrate. In the first case, we considered a plan wave excitation. We then calculate the scattered field in this situation. With such a setup, only bright modes are accessible. In the second setup, we placed a dipole 50 nm next to the nanowire. We then place a monitor 10 nm above the nanowire and recorded the intensity of the field in this monitor as a function of the frequency, thus revealing the existence of surface phonon polaritons.

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**Author contributions:** P.-A.M. developed the model, conceived and performed the experiments. S. L. and M.B. prepared the samples. P.-A.M and K.Y.L. performed the simulations. P.-A.M., D.F.-S. and A.Y. analyzed the data. P.-A.M wrote the manuscript and all authors approved the final version.

**Figures and Tables**
Fig. 1. Generating surface phonon polaritons. (a) Schematic representation of the transient depletion field screening responsible for the generation of surface phonon polaritons. (b) Oscillatory component of the transient reflectivity obtained on InP nanowires with a pump and probe wavelength of 550 and 720 nm, respectively. Inset: transient reflectivity before subtraction of the electronic and thermal contributions. (c) Fourier transform of the transient reflectivity (Blue line) and Raman spectrum (Red line) obtained on the InP nanowires.
**Fig. 2.** Doping concentration dependence. (a) Fourier transforms of the transient reflectivity obtained on nanowires with various doping concentrations. (b) Amplitude of coherent vibrations at different frequencies as a function of doping concentration.

**Fig. 3.** Surface phonon polaritons modes. Upper panel: Fourier transform of the transient reflectivity signals obtained on InP nanowires in air and in CH$_2$Cl$_2$. Lower panel: simulation of the absorption by an InP nanowire at THz frequency for an incident plane wave in air (dashed blue line), a dipole located in the vicinity of the nanowire in air (solid blue line), and for a dipole in CH$_2$Cl$_2$ (solid red line).

**Supplementary Materials**

**Supplementary Note 1**

The temporal evolution of the coherent atomic vibration $Q_j$ along the direction $j$ can be described by:

$$\mu (\ddot{Q}_j + \Gamma \dot{Q}_j + \omega^2 Q_j) = F(t)$$  \hspace{1cm} (S1)

Here $F(t)$ can take multiple form due to the various possible interactions with the pump pulse. In the following, we review the most important ones. First, coherent atomic displacement in the $j$ crystal direction can be due to second order nonlinear effects. In that case:
\[ F(t) = -\frac{e^*}{\varepsilon_\infty \varepsilon_0} \chi_{jk}^{(2)} E_k E_l \]  

(S2)

with \( E_k \) and \( E_l \) components of the pump pulse, \( e^* \), the effective lattice charge, \( \varepsilon_0 \), the vacuum permittivity, \( \varepsilon_\infty \), the high frequency dielectric function and \( \chi_{jk}^{(2)} \) is the second order susceptibility.

We then consider a third order process. Here, the surface field \( E_S \) contributes to the generation of vibrations:

\[ F(t) = -\frac{e^*}{\varepsilon_\infty \varepsilon_0} \chi_{jkl}^{(3)} E_k E_l E_S \]  

(S3)

where \( \chi_{jkl}^{(3)} \) is the third order susceptibility.

Then we need to consider the force exerted by the current \( J_j \) along the direction \( j \). In the presence of a surface depletion field, due to the Fermi level pinning at the surface, pump absorption results in generation of electrons and holes that are spatially separated under the influence of this surface field, resulting in a current \( J_j \). Subsequently, the surface field is reduced due to screening by photogenerated charges and the atoms are driven out of their equilibrium position. The associated force is given by:

\[ F(t) = -\frac{e^*}{\varepsilon_\infty \varepsilon_0} \int_{-\infty}^{t} J_j(t') dt' \]  

(S4)

Since the current is proportional to the surface electric field and the density of photoexcited carriers, we can express (S4) as:

\[ F(t) = -\alpha I_{\text{pump}} E_S \]

where \( \alpha \) is a constant and \( I_{\text{pump}} \) is the intensity of the pump pulse.

Other mechanisms can be responsible for the generation of coherent vibrations. For instance, charge transfer from the nanowires to the adsorbates and vice versa is modifying the local density of carriers and drives atoms out of their equilibrium position. The transition from the ground state to the excited state will similarly modify the bonding between atoms and change their equilibrium position.

**Supplementary Note 2**

Due to the pump pulse, multiple coherent vibrations are generated. These vibrations are associated to an electric field, \( E_V \):

\[ E_V = E_0 \cos (\omega t + \varphi)e^{-\frac{t}{\tau}} \]

with \( \omega \) the frequency of the vibrational mode, \( \varphi \), its phase, and \( \tau \), the lifetime of the vibration. The signal we detect is resulting from the interaction of these vibrations with the Gaussian probe pulse, \( E_P \). Here, we limit our investigation to the second and third order interactions:

\[
\Delta R(t) \propto \int_{-\infty}^{+\infty} \left| E_P(t') + E_P(t') E_V(t + t') + E_S E_P(t') E_V(t + t') \right|^2 dt'
\]

\[
= \int_{-\infty}^{+\infty} \left| E_P e^{i(\omega_1 t' + \varphi_1)} e^{-\frac{1}{2} \left( \frac{t'}{\tau} \right)^2} \right|^2 dt'
\]

\[
+ \chi^{(2)} E_P E_0 e^{i(\omega_1 t' + \omega(t + t') + \varphi_1 + \varphi)} e^{-\frac{1}{2} \left( \frac{t + t'}{\tau} \right)^2} \frac{t + t'}{\tau} \]

\[
+ \chi^{(3)} E_P E_0 E_S e^{i(\omega(t + t') + \varphi_1 + \varphi)} e^{-\frac{1}{2} \left( \frac{t + t'}{\tau} \right)^2} \frac{(t + t')^2}{\tau^2} \]

\]}
Since we are only concerned with transient signal, we can simplify this expression by only conserving the lowest order terms with a time dependence in the cross product. We then obtain:

$$\Delta R(t) \propto \int_{-\infty}^{+\infty} \chi^{(2)} |E_{p0}|^2 E_0 \cos (\omega (t + t') + \varphi) e^{-\frac{(t')^2}{\Delta t}} + \chi^{(3)} |E_{p0}|^2 E_0 E_s \cos (\omega (t + t') + \varphi) e^{-\frac{t + t'}{\tau}} dt'$$

In our experiments, the vibration frequency is such that $\omega_2 \Delta t \ll 1$, as a consequence, we can consider that the value of this cosine is constant over the duration of the probe pulse. We thus have:

$$\Delta R(t) \propto \chi^{(2)} |E_{p0}|^2 E_0 \cos (\omega t + \varphi) e^{-\frac{t}{\tau}} + \chi^{(3)} |E_{p0}|^2 E_0 E_s \cos (\omega t + \varphi) e^{-\frac{t}{\tau}}$$

**Supplementary Figure 1**

![Supplementary Figure 1](image)

**Fig. S1**: Comparison of the coherent contributions to the transient reflectivity for various polarizations of the pump and probe beam, with a pump wavelength of 550 nm and a probe wavelength of 720 nm. These experiments are performed at grazing angle. The orientation given in the figure corresponds to the angle between the polarization and the axis of the nanowires.

**Supplementary Figure 2**
Fig. S2: Distribution of the z component of the electric field for the (a) monopole (9.1 THz), (b) transverse dipole 1 (9.8 THz) and (c) transverse dipole 2 (10. THz).