

Surface Phonon Polariton Ellipsometry

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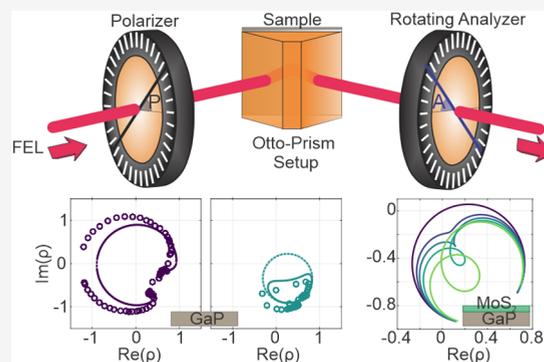
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ABSTRACT: Surface phonon polaritons (SPhPs) have become a key ingredient for infrared nanophotonics owing to their long lifetimes and the large number of polar dielectric crystals supporting them. While these evanescent modes have been thoroughly characterized by near-field mapping or far-field intensity measurements over the past decade, far-field optical experiments also providing phase information are less common. In this Article, we study surface phonon polaritons at the gallium phosphide (GaP)–air interface in the momentum domain using the Otto-type prism coupling geometry. We combine this method with spectroscopic ellipsometry to obtain both amplitude and phase information on the reflected waves across the entire reststrahlen band of GaP. By adjusting the prism–sample air gap width, we systematically study the dependence of the ellipsometry parameters on the optical coupling efficiency. In particular, we show that the combined observation of both ellipsometry parameters, amplitude and phase, provides a powerful tool for the detection of SPhPs, even in the presence of high optical losses. Finally, we theoretically study how surface phonon polariton ellipsometry can reveal the emergence of vibrational strong coupling through changes in the topology of their complex plane trajectories, opening up a new perspective on light–matter coupling.

KEYWORDS: light–matter coupling, prism coupling, vibrational strong coupling, gallium phosphide, Stokes vectors, spectroscopic ellipsometry



INTRODUCTION

Phonon polaritons (PhPs) are light–matter electromagnetic waves that arise in polar crystals from the hybridization of infrared (IR) photons with IR-active phonons. The research field has grown out of efforts to explore the possibilities of nanophotonics beyond the limits imposed by plasmonics¹ by extending the available spectral range for polaritonic modes into the IR and THz, while dramatically reducing optical losses thanks to the long lifetimes of phonons (typically on the picosecond time scale).^{2–4} Furthermore, PhPs have attracted much attention in recent years due to the high directionality resulting from the inherently anisotropic optical response of low-symmetry crystals, which are natural platforms for these types of modes.^{5,6} In addition, the wide variety of crystals available in nature allows to explore the extreme multifacetedness of PhPs,⁷ paving the way for the development of a plethora of applications for advanced nanophotonic-based devices.⁸

The coupling between photons and phonons is responsible for the formation of bulk PhPs and leads to an avoided crossing in their dispersion relation. This, in turn, results in the formation of a spectral region known as reststrahlen band (RB), bounded by the transversal optical (TO) and longitudinal optical (LO) phonon frequencies, where light propagation within the crystal bulk is prohibited.^{9–11} This frequency interval is therefore characterized by a near-unity

reflectance, reminiscent of the optical response of metals below the plasma frequency.² In polar crystals, the Rabi frequency Ω_R for bulk phonon polaritons, related to the RB width through $\Omega_R = \sqrt{\omega_{LO}^2 - \omega_{TO}^2}/2$, is generally in the order of 10 to 80% of the TO frequency,^{12,13} which naturally places PhPs in the ultrastrong light–matter coupling regime.

In recent years, much effort was dedicated to modulating light–matter coupling, e.g., with different types of photonic resonators,¹⁴ with crystals of plasmonic nanoparticles¹² or with molecular switches embedded in optical microcavities.¹⁵ However, achieving such modulation by employing PhPs in polar crystals is not so easy from an experimental point of view. It requires manipulating the LO–TO splitting by irreversibly changing the material properties, e.g., by isotopic substitution¹⁶ or, alternatively, employing heterostructured metamaterials.^{17–19}

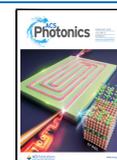
Interestingly, due to their “metal-like” optical behavior in the RB, polar dielectrics can support evanescent surface waves

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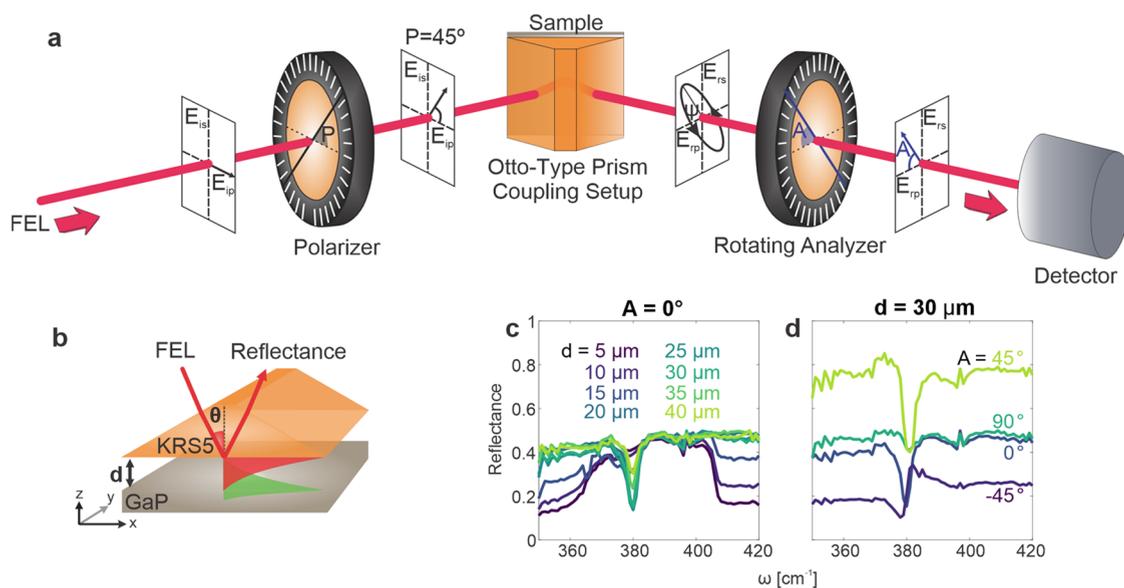


Figure 1. Experimental setup for spectroscopic ellipsometry measurements in an Otto-type prism coupling configuration. (a) Schematic of the rotating-analyzer ellipsometry (PSA_R) setup employed in the experiment, consisting of two wire grid polarizers and the prism–sample system. (b) Otto-type prism coupling geometry employed for the excitation and detection of surface phonon polaritons at the interface between gallium phosphide and air. The red- and green-shaded areas denote the evanescent waves for TIR and SPhP, respectively. (c) Experimental far-infrared reflectance spectra recorded at eight different air gap widths for a fixed analyzer angle, $A = 0^\circ$. (d) Experimental reflectance spectra recorded at four different analyzer angle configurations for a fixed air gap width of $d = 30 \mu\text{m}$.

known as surface phonon polaritons (SPhPs) in that spectral region. The evanescent nature of SPhPs exhibiting momenta outside the light cone prevents their direct optical excitation from the free space. However, it is possible to excite SPhPs within the RB employing dedicated experimental schemes to overcome the momentum mismatch with free-space radiation.^{6,18,20–24} Recent studies have investigated different surface modes in polar dielectric crystals and heterostructures with intensity measurements enabled by grating^{23,24} or prism^{6,18,21,22} coupling techniques. In particular, when arranged in the so-called Otto geometry,²⁵ prism coupling provides unsurpassed control over the excitation efficiency of the SPhPs.^{11,20} Therefore, Otto-type prism coupling offers a unique platform for the investigation of light–matter coupling in polar crystals.

In this work, we combine Otto-type prism coupling with spectroscopic ellipsometry, a widespread technique that is typically employed to derive the complex dielectric tensors of crystals.²⁶ This combined approach enables the acquisition of both amplitude and phase information on SPhPs here exemplified in the far-infrared for gallium phosphide (GaP). While the optical response of this crystal is already well-known,²⁷ to the best of our knowledge, no phase-resolved optical response of its surface modes has been reported. By means of this hybrid method, which we call “surface phonon polariton ellipsometry”, we measure the complex-valued ellipsometry parameter ρ for various optical coupling efficiencies, as controlled in the experiment by varying the air gap width between the prism and the sample. The results show that the representation of the quantity ρ in the complex plane provides a unique perspective on optical coupling phenomena, e.g., by allowing a complementary visualization of the critical coupling condition.^{11,20} We compare these data with transfer matrix simulations of free-space excited GaP, where no evanescent waves emerge, providing complementary insight into light–matter coupling both in free space and

mediated by evanescent waves. Finally, we theoretically apply our method to study phonon–polariton strong coupling using thin films of MoS₂ on GaP as a potential vibrational strong coupling platform and predict a change in topology of the complex plane trajectories of ρ by varying the MoS₂ thickness, conceptually similar to previous ellipsometry work in the visible.¹⁵ From a broader perspective, experimental access to the optical phase of surface modes opens up new ways of characterizing strong light–matter coupling, the emergence of SPhPs within the RB, and the coupling of these surface modes to other resonances.

EXPERIMENTAL RESULTS

We applied far-IR spectroscopic ellipsometry for phase-resolved investigations of SPhPs on the surface of a 1 mm thick GaP single crystal (Mateck GmbH). In order to overcome the momentum mismatch between the incident light and the SPhP for excitation of the surface modes, we employed a high refractive index thallium bromo-iodide (KRS5) prism arranged in the Otto-type prism coupling geometry.^{9,11,20,25} This technique allows us to deterministically tune the evanescent in-plane momentum of the excitation by changing the incidence angle of the laser beam, as well as the coupling efficiency by adjusting the spacing d between the prism and the sample. This air gap width is precisely monitored by means of white-light interferometry.²⁸ When far-IR radiation is incident on the prism–air interface at an angle θ larger than the critical condition for total internal reflection (TIR), excitation of SPhPs in the underlying substrate can occur. This is schematically illustrated in Figure 1b by the overlap between the red- and green-shaded areas, which denote the evanescent waves for total internal reflection and a SPhP, respectively. In our experiment, we performed narrow-band (<0.5% bandwidth) excitation spectroscopy in the far-IR region of the electromagnetic spectrum (350–420

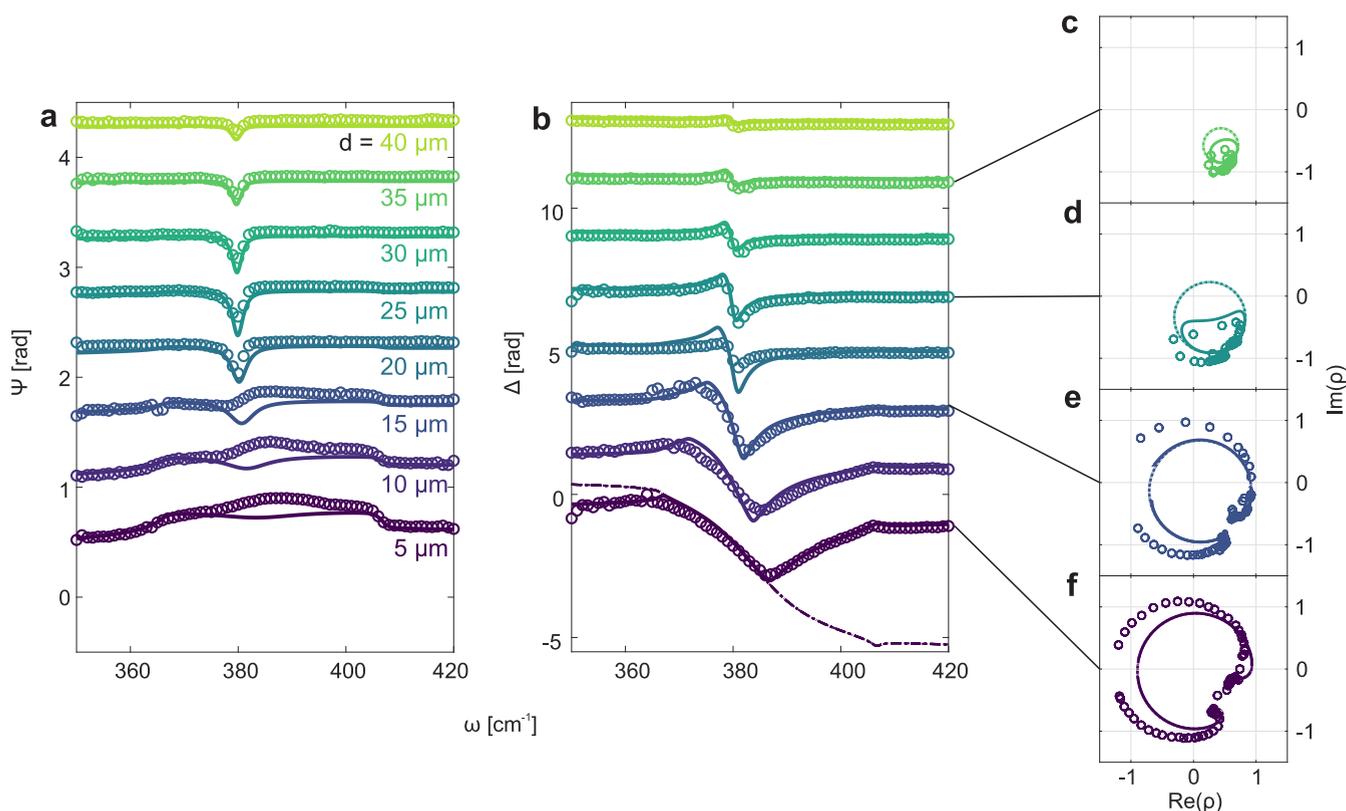


Figure 2. Ellipsometry parameters $\Psi(\omega)$ and $\Delta(\omega)$ extracted from experimental data (circles) and TM simulations (solid and dashed lines). (a, b) Spectra of the amplitude Ψ (a) and phase difference Δ between s- and p-polarization components (b) for selected gap widths d . When the TM simulations were performed, the presence of a thallium bromiodide (KRS5) prism was considered while setting up the material system. An offset was added both to the incidence angle and the gap width, resulting in the following choice of parameters for the simulated spectra: $\theta_{\text{sim}} = 26.55^\circ$ and $d_{\text{sim}} = 10, 15, 20, \dots \mu\text{m}$. (c–f) Complex plane representation of ρ , plotted as a function of frequency. The simulations shown in the panels were obtained by using two different methods. The dashed lines have been plotted directly from the ratio of the Fresnel reflection coefficients as described by eq 2. This also applies to the dashed purple line in panel b, which is mirrored for the purpose of display (the mirroring is responsible for the mismatch of the two curves at $\omega < 370 \text{ cm}^{-1}$). On the other hand, the solid lines are the result of simulations applied to mimic the PSA_R setup, taking additionally into account the broadening of the FEL frequency (as explained in detail in the SI).

cm^{-1}) by utilizing the IR free-electron laser at the Fritz-Haber Institute (FHI-FEL)²⁹ as tunable IR light source.

In a typical reflectance measurement at the GaP surface in the Otto geometry, the SPhP resonance results in a dip in the reflectance spectrum with the dip magnitude representing the SPhP amplitude.^{11,27} To obtain the phase information, however, we employed a home-built rotating-analyzer ellipsometry (also called polarizer-sample-rotating analyzer, PSA_R) setup. As depicted in Figure 1a, the setup consists of two wire-grid polarizers in addition to the prism–sample system. The incident p-polarized far-IR radiation is converted by a linear polarizer, which rotates the polarization by an angle P of 45° into a linear combination of p- and s-polarization components with zero phase offset. Then, the light encounters the Otto geometry, where a nonzero relative phase Δ between the two components arises due to the different Fresnel reflection coefficients for the two polarization components at the interface between the GaP substrate and air, in general, leading to an elliptical polarization of the reflected beam. To fully characterize the polarization of the reflected beam, reflectance spectra at four analyzer settings, $A = 0^\circ, 90^\circ, 45^\circ$, and -45° , are recorded with a pyroelectric detector for various air gap widths at a fixed incidence angle θ of 27° . The complete set of these reflectance spectra is available in the Supporting Information (Figure S1a–d).

In Figure 1c we show the experimental data recorded at $A = 0^\circ$, which illustrates the p-polarized component of the elliptically polarized light reflected off the Otto system. The data is referenced to unity reflectance at total internal reflection with very large ($\approx 100 \mu\text{m}$) air gap width and renormalized to the maximum reflectance obtained from simulations (for further details on the data treatment see SI, Section 1). In the overcoupled regime, i.e., at small prism–sample distances, we can clearly recognize the highly reflective RB region of GaP. In this frequency range, where light propagation inside the crystal is prohibited, the evanescent p-polarized waves at the prism–sample gap couple to SPhPs, resulting in pronounced dips in the reflectance spectra, as visible in the green or turquoise curves in Figure 1c ($d = 25$ and $30 \mu\text{m}$, respectively). Notably, Maxwell’s equations do not predict s-polarized near-fields in the case of optically isotropic crystals such as GaP.³⁰ Hence, when comparing the reflectance spectra at different analyzer settings for an air–sample spacing, $d = 30 \mu\text{m}$ in Figure 1d, we do not expect to observe any SPhP excitation in the turquoise curve ($A = 90^\circ$), which corresponds to the spectrum of the s-polarized component, where indeed the SPhP resonance dip is largely suppressed in the experiment. The small remnant feature may arise from imperfect polarization states.

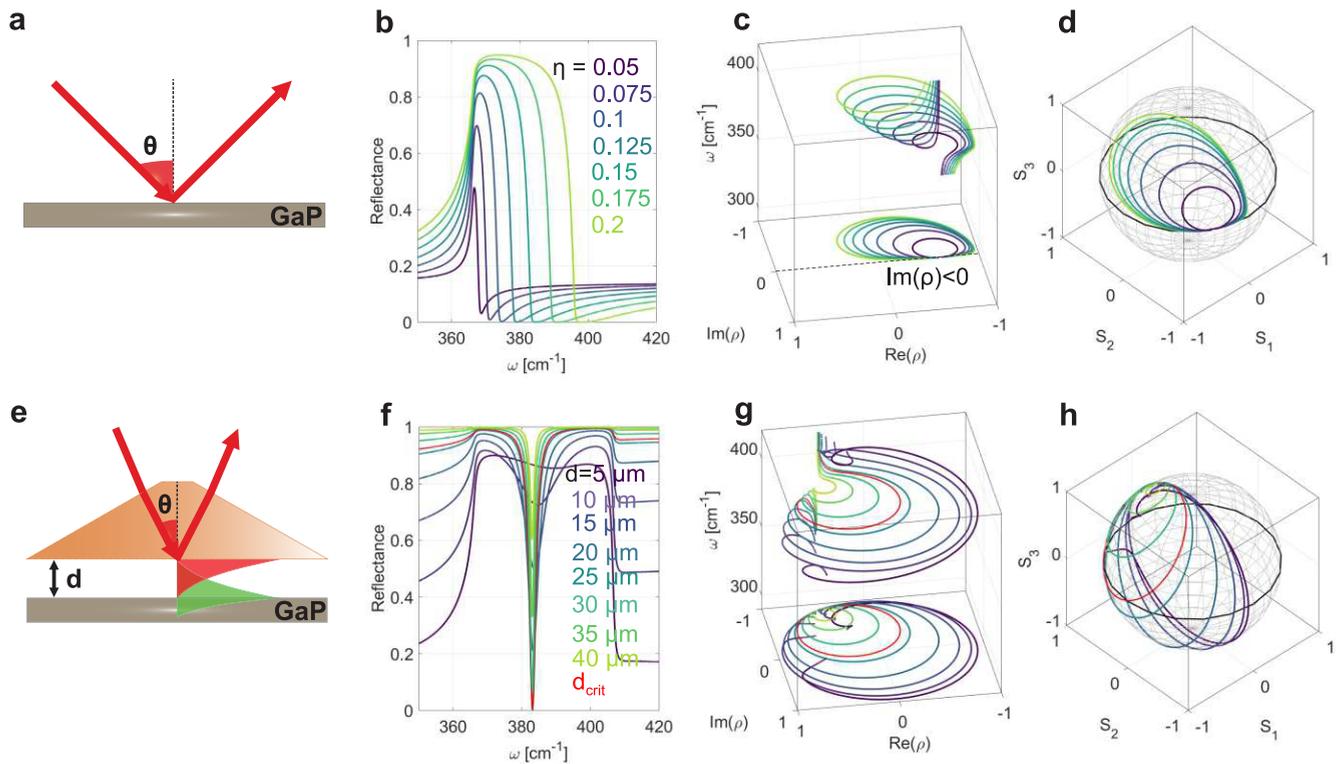


Figure 3. TM simulations of ellipsometry parameter for the GaP–air interface in free-space (upper row) and in a total internal reflection-based illumination scheme (lower row). (a, e) Sketches illustrating the reflection scheme in free-space (a) and in the prism coupling geometry (e). (b, f) Simulated reflectance spectra around the reststrahlen band (RB) of GaP. The simulations are performed considering incidence angles θ of 45° (b) and 27° (f). The various curves shown in the panels correspond to different normalized coupling strengths η (b) and gap widths d (f). (c, g) 3D plots of ρ vs ω and corresponding projections in the xy -plane of loops in the complex plane representation. (d, h) Poincaré-sphere representation of the polarization state of the light reflected off the air-GaP interface, without (d) and with (h) the prism. The red curves in panels (f)–(h) correspond to the critical coupling condition and were calculated by assuming a prism-sample spacing of $26.53 \mu\text{m}$. This value was obtained numerically from the Parratt recursion formula for a multilayer system after setting the condition for critical coupling: $\Im(\rho) = \Re(\rho) = 0$. The black line at the equator in panels (d) and (h) is marked for reference.

All four reflectance measurements displayed in Figure 1d are required to experimentally obtain the four-component Stokes vector \vec{S} .³¹ In fact, only the first three Stokes vector components can be measured directly in our PSA_R setup, as they are obtained from the quantities plotted in Figure 1d, as follows:

$$\begin{aligned} S_0 &= R_{A=0^\circ} + R_{A=90^\circ} \\ S_1 &= R_{A=0^\circ} - R_{A=90^\circ} \\ S_2 &= R_{A=45^\circ} - R_{A=-45^\circ} \end{aligned} \quad (1)$$

S_3 , which defines the latitude in the Poincaré sphere representation and contains information about the degree of ellipticity and the chirality, is derived from the other components by assuming totally polarized light as $S_3 = \sqrt{S_0^2 - S_1^2 - S_2^2}$.³¹ From the Stokes vector, we extract the ellipsometry parameters Ψ and Δ , which correspond to amplitude and phase, respectively, of the complex ratio $\rho = r_{pp}/r_{ss}$, where r_{pp} and r_{ss} are the Fresnel reflection coefficients for p- and s-polarization, respectively

$$\rho = \frac{r_{pp}}{r_{ss}} = \tan(\Psi)e^{i\Delta} \quad (2)$$

The quantities Ψ and Δ are related to the Stokes parameters as follows:³¹

$$\Psi = -\frac{1}{2} \arccos\left(-\frac{S_1}{S_0}\right) \quad (3)$$

$$\Delta = \begin{cases} \arctan\left(-\frac{S_3}{S_2}\right) & \text{for } \cos(\Delta) > 0, \\ \arctan\left(-\frac{S_3}{S_2}\right) + \pi & \text{for } \cos(\Delta) < 0, \sin(\Delta) \geq 0, \\ \arctan\left(-\frac{S_3}{S_2}\right) - \pi & \text{for } \cos(\Delta) < 0, \sin(\Delta) < 0 \end{cases} \quad (4)$$

More details about spectroscopic ellipsometry in this particular configuration can be found in ref 31.

The spectra of the ellipsometry parameters Ψ and Δ extracted from the experimental data are shown as waterfall plots in Figure 2a,b (circles) for various air-gap widths d . In Figure 2c–f, we show the corresponding representation of ρ in the complex plane for selected values of d . In general, plotting ρ in the complex plane allows us to look at the SPhP excitation from an unusual perspective that is not possible with traditional intensity measurements. These data are overlaid with the corresponding transfer matrix (TM) simulations³² (solid lines). As already extensively discussed in a previous work by Passler et al.,²⁰ the gap dependence of the polariton feature's prominence in the reflectance spectrum exhibits a

critical behavior that is reproduced here in the amplitude Ψ data. In Figure 2a, we observe a faint dip at the smallest gap width of $5 \mu\text{m}$, where the coupling efficiency is strongly diminished due to the high radiative losses of the SPhP evanescent tail back into the prism. For larger gaps, an increasingly prominent and narrow dip emerges in the spectrum, until the condition of critical coupling is reached at $d_{\text{crit}} \approx 25 \mu\text{m}$, corresponding to the optimal distance at which the incident light is completely absorbed by the SPhP. At a prism–sample spacing larger than the critical gap width ($d > d_{\text{crit}}$), we access the ‘undercoupled’ regime, where the small overlap between the two evanescent waves shown in the schematics of Figure 1b prevents an efficient SPhP excitation. This results in a shallower, yet narrow dip in the spectrum of Ψ (see, e.g., the light turquoise and green curves in Figure 2a, $d = 35$ and $40 \mu\text{m}$). Due to irregularities in the shape of the baseline (see SI, Section S1), the agreement between experiment and simulation is not optimal at small gaps but improves significantly with increasing gap width and is excellent at the critical coupling condition.

A similar critical behavior is observed for the phase Δ (Figure 2b), as well as in the selected plots of ρ in the complex plane (Figure 2c–f). The absorption of IR light results in dips in the amplitude spectra (Figure 2a), which translate into phase jumps in Δ (Figure 2b) and into quasi-circular trajectories in the complex plane representation of ρ (Figure 2c–f). At small gaps in the overcoupled regime, the phase changes nearly linearly across the full RB over a total range of 2π , corresponding to the full loop in Figure 2f. This behavior is displayed by the dashed lines in Figure 2b–f (in panel b, only one ‘unfolded’ Δ -spectrum has been reported, which has been mirrored for the purpose of display). Notably, the experimental data in this case are folded since the PSA_R method, according to eq 4, cannot resolve the ambiguity in the sign of S_3 , due to $-\pi < \Delta < 0$ ³¹ (see SI, section S2 for an extensive discussion). Upon increasing the air gap, the dispersive region of Δ shrinks and the curve steepens to form a Lorentzian-like SPhP resonance, with the steepest slope emerging at critical coupling (see Δ_{theory} in Figure S3c). The critical coupling condition is hence characterized by the highest gradient of the Δ -spectra at the SPhP resonance frequency (see the turquoise–green curve at $d = 25 \mu\text{m}$, in Figure 2b), which corresponds to the point where the loop formed by ρ intersects with the origin in the complex plane. Notably, close to the critical coupling condition (Figure 2d), the finite spectral line width of our FEL results in a distortion of the signals leading to a deformation of the loop (see Figure S4). For even larger gaps, the magnitude of the resonance diminishes, associated with a further shrinking of the loop size in the complex plane. In this case, the trajectories are defined only in half of the complex plane (when $\Im(\rho) < 0$) such that Δ no longer exhibits a 2π step across the RB.

Notably, the critical behavior visible in the gap width dependence of Ψ and Δ , when considered independently in panels a and b, transforms into a monotonic change of the loop radius in the complex plane. A very similar behavior of RB-induced loops of ρ in the complex plane can be found when analyzing free-space infrared spectroscopic ellipsometry data of polar crystals such as ZnO³³ or alumina.³⁴ However, in free-space ellipsometry, the loops only cover a half-space of the complex plane corresponding to a π -step in Δ only. In order to better understand these complex plane loops conceptually, we will analyze the different scenarios theoretically in the following.

COMPLEX PLANE LOOPS IN POLARITON ELLIPSOMETRY

To gain a deeper understanding of the loops of ρ in the complex plane, we now theoretically compare the Otto-type prism coupling configuration with free-space excitation of a polar crystal using TM calculations, see Figure 3. For the free-space case, we assume that light is incident on the air–sample interface at an angle of 45° (Figure 3a). In this picture, the strong TO phonon resonance couples to the incoming light, which is then responsible for the excitation of the upper or the lower bulk phonon polariton (BPhP) branch. The dielectric permittivity of the substrate can be described by means of a classical Lorentz model with an oscillator strength g :

$$\epsilon(\omega) = \epsilon_\infty + g \frac{\omega_{\text{TO}}^2}{\omega_{\text{TO}}^2 - \omega^2 - i\Gamma\omega} \quad (5)$$

By modifying g , it is possible to tune the Rabi splitting $2\Omega_{\text{R}}$ of the system, since $g = \frac{4\epsilon_\infty\Omega_{\text{R}}^2}{\omega_{\text{TO}}^2}$, and thus the normalized coupling strength $\eta = \frac{\Omega_{\text{R}}}{\omega_{\text{TO}}}$.¹² Figure 3b shows the reflectance spectra calculated for various values of η , from strong to ultrastrong ($\eta > 0.1$) light–matter coupling regimes.^{14,35} We note that using the Lorentz oscillator model in the ultrastrong coupling regime corresponds to the Hopfield model of light–matter coupling, that includes counter-rotating and higher-order terms in the Hamiltonian.¹² More details on the simulations are available in SI, Section S3. In these plots, the high-reflectance spectral region becomes broader with increasing normalized coupling strengths η . Notably, for all the curves there is a frequency range where the real part of the dielectric permittivity acquires negative values, leading to the buildup of a RB in all the cases analyzed here. If we study the frequency dependence of ρ and visualize it in a 3D plot, as shown in Figure 3c, we observe a helicoidal shape that results in loops when projected onto the complex ρ plane. The loop size increases with η . For this system, ρ can undergo a maximum phase jump of π , which causes the asymmetric trajectories to be confined to the negative half of the plane (where $\Im(\rho) < 0$). This behavior is typical of a dielectric environment in the presence of a resonance.³⁶

An alternative way of presenting the loops is to plot the polarization state of the light reflected off the air–GaP interface on the Poincaré sphere (Figure 3d). Under the assumption of totally polarized light, the Stokes vector traces squeezed loops in the northern hemisphere. This visualization method helps to reveal the physical meaning of the trajectories, in particular showing that the strong coupling of the light to a dipolar material resonance is not sufficient to induce a change in the handedness of the reflected radiation (see SI, Section S4 for a comparison between the two visualization methods). The fact that S_3 is always positive determines that the light is right-elliptically polarized over the entire frequency range considered, and for all values of η .

The picture described above does not include SPhPs. To do so, we now add a high-refractive-index prism as sketched in Figure 3e in the TM simulations. In this scenario, the surface mode emerges as a dip in the reflectance spectra in Figure 3f. Like in the experiments shown in Figure 2, we tune the air gap width between the prism and the sample to modulate the coupling efficiency. The red curve corresponds to the critical

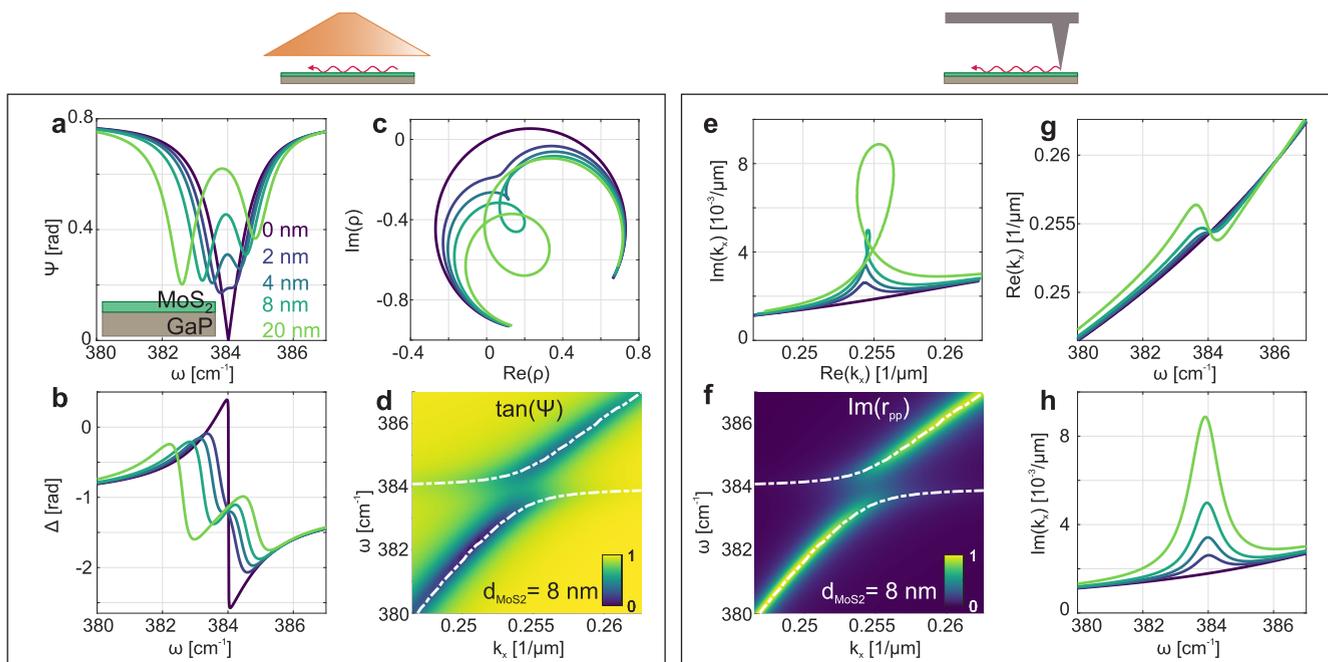


Figure 4. Transition from weak to strong coupling in a MoS₂/GaP system for different MoS₂ thicknesses. The large black boxes group the panels according to the two different methods for studying strong coupling: TIR and tip-based approaches on the left and right, respectively, as shown in the sketches above. (a–c) Simulated ellipsometry parameters for a material system of the type depicted in the inset of panel a. The different curves are obtained by varying the thickness of the MoS₂ thin slab, see labels. The simulations were performed by assuming an incidence angle $\theta = 27.165^\circ$ and a gap $d = 24.95 \mu\text{m}$. (d, f) Simulated reflectivity maps derived from the magnitude of ρ , i.e., $\tan(\Psi)$, and the imaginary part of the reflection coefficient for p-polarized light, $\Im(r_{pp})$, normalized to its maximum, respectively. Both maps are obtained by assuming a MoS₂ thickness of 8 nm. The simulations are overlaid with semianalytical dispersion curves (dashed white lines); see SI Section S7. (e,g,h) Real (g) and imaginary (h) parts of the in-plane wave vector k_x obtained from the peak positions and line widths, respectively, of horizontal line cuts through the dispersion maps (exemplified in panel f for $d = 8 \text{ nm}$). While in panels g and h, $\Re(k_x)$ and $\Im(k_x)$ are plotted against ω , panel e shows a plot of the imaginary part against the real part.

coupling condition, where every photon impinging on the surface is absorbed at the SPhP resonance.

Furthermore, the complex ratio ρ is plotted in 3D as a function of frequency (analogous to Figure 3c), as shown in Figure 3g for various gap widths. The projections of ρ in the complex plane are quasi-circular trajectories that undergo a transition from the undercoupled to the overcoupled regime, crossing the origin of the complex plane at the critical coupling condition (red curve). This is in stark contrast to the loops discussed in the panel above (Figure 3c) obtained from the free-space reflection scheme, which solely emerge in the negative half-space of the complex plane. As observed experimentally, when a KRSS prism is brought close enough to the sample in the overcoupled regime, the phase Δ covers the full range of 2π (see Figure S3c), which causes the loops across the entire complex plane. The experimental results shown in Figure 2c–f, despite some experimental limitations, confirm this transition.

Interestingly, the data show that ρ crosses the origin of the complex plane even in the presence of high radiative losses. Consider for instance, the amplitude Ψ measured at $d = 5 \mu\text{m}$ (Figure 2a), where the dip is broad and hardly recognizable. The corresponding loop plotted in Figure 2f, however, has a large radius and extends over the entire complex plane. As a complementary picture, Figure 3h provides an overview of the polarization state of the reflected radiation. Notably, the Stokes vector traces circular trajectories on the Poincaré sphere that cross the equator at small gap widths. This indicates that an efficient surface mode's excitation, independent of the radiative

losses, is responsible for a change of handedness in the polarization state of the reflected beam. We note, however, that also other factors may cause a change of handedness in the three-layer prism-gap-sample arrangement; see SI, section S6 for more details.

While manipulating the LO–TO splitting (e.g., by changing the light-matter coupling η) in a bulk crystal is not experimentally feasible without structurally modifying the material properties, the Otto-type prism coupling technique offers a unique noninvasive tunability of the optical coupling efficiency. We show that, in combination with spectroscopic ellipsometry, this approach enables advanced control over the SPhP excitation, opening new pathways for the study of the light-matter coupling and the emergence of surface modes in the photonic bandgap.

■ VIBRATIONAL STRONG COUPLING

The unique perspective on optical coupling phenomena arising in the complex plane of the ellipsometry parameter ρ may also provide opportunities for vibrational strong coupling for infrared sensing applications.^{23,37,38} To explore these phenomena using polariton ellipsometry, we theoretically consider in the following a simple model system comprising a very thin film of the two-dimensional van der Waals crystal MoS₂ placed on top of a GaP substrate. MoS₂ exhibits a weak IR-active phonon resonance at $\omega_{\text{TO}} = 384 \text{ cm}^{-1}$ within the SPhP band of GaP.³⁹ Thus, we can expect a strong coupling of the GaP SPhP to the MoS₂ phonon that can be characterized in the Otto

configuration. A schematic of the material stack is shown in the inset of Figure 4a.

TM simulations were performed by varying the thickness of the MoS₂ layer from 0 to 20 nm at a fixed angle of incidence and at the critical coupling condition for the GaP SPhP without MoS₂, see Figure S8 for details. The angle of incidence was chosen such that the SPhP resonance matched exactly with the MoS₂ phonon ($\theta = 27.165^\circ$). The resulting ellipsometry parameters Ψ and Δ (derived from $\rho = r_{pp}/r_{ss}$) are plotted in Figure 4a,b. Although the dip in Ψ (the phase jump in Δ) shows a broadening and a deformation (a flatter slope and a break in the monotonicity) already for a 2 nm thick MoS₂ slab, the onset of strong coupling can be observed only at a thickness of 4 nm (see SI, section S7 for a more detailed explanation). As the MoS₂ slab thickness increases, two dips in the amplitude Ψ appear and become increasingly distinct in Figure 4a. For the phase Δ in Figure 4b, the interaction between the two modes manifests itself in the emergence of two Lorentzian-like resonances that become gradually more spectrally separated (see e.g. turquoise and green lines in Figure 4a,b). The amplitude and phase information, when considered independently, do not provide any robust criterion to characterize the strong coupling regime without first quantifying the Rabi splitting and comparing it to the line widths of the uncoupled resonances.

However, the combined observation of both ellipsometry parameters (Ψ and Δ) in the complex plane visualization of ρ provides a more suitable tool to detect the onset of strong coupling,¹⁵ see Figure 4c. In these plots, the transition from weak to strong coupling with an increasing thickness is manifested as a change in topology. At $d_{\text{MoS}_2} = 2$ nm, the area enclosed by the primary loop, which, as discussed in detail in the previous section, represents the signature of the surface phonon polariton of GaP, reduces, while its continuity is interrupted by a kink. At the onset of strong coupling, the dimple transforms into a secondary loop right around $d_{\text{MoS}_2} = 4$ nm, which becomes more pronounced for thicker MoS₂ slabs ($d_{\text{MoS}_2} = 8$ and 20 nm). We additionally reproduced the strong coupling onset using the Hopfield model, see SI, section S7, which further supports that the strong coupling transition indeed happens at $d_{\text{MoS}_2} = 4$ nm. A similar topological transition in the optical response has been recently observed with spectroscopic ellipsometry in a coupled system consisting of optical microcavities and organic molecules.¹⁵

To confirm that our model system has indeed already reached the strong coupling regime at $d_{\text{MoS}_2} = 8$ nm, we plot the dispersion in Figure 4d. There we show the TM-simulated color map of $\tan(\Psi)$. The strong coupling with the associated avoided crossing in the dispersion relation is reproduced by the overlaid semianalytical model (white dashed lines); see SI, section S7 for details. The upper and lower polariton branches are the eigenvalues of the Hopfield Hamiltonian, derived by assuming a coupling strength g larger than the system's losses. Thus, surface phonon polariton ellipsometry promises to emerge as a powerful tool to study vibrational strong coupling, since it enables the observation of the transition into strong coupling as a change in the topology of ρ , providing a complementary platform for vibrational strong coupling employing SPhPs.^{23,37}

Interestingly, a similar approach of exploring strong coupling through loops in the complex plane was recently discussed for

the complex-valued in-plane polariton wave vector k_x .^{40,41} In this case, simultaneous near-field measurements of the polariton wavelength and propagation length also enable a complex plane representation, in which strong coupling results in the buildup of a loop.⁴⁰ For a direct comparison to our ellipsometry approach, we extracted the respective quantities from TM simulations of the same system; see Figure 4e–h. Trajectories of the complex-valued wave vector are shown in Figure 4e. The real and imaginary parts of k_x are extracted from the peak positions and line widths, respectively, of horizontal cuts through dispersion maps of $\Im(r_{pp})$, as exemplified in Figure 4f for $d_{\text{MoS}_2} = 8$ nm. The results for $\Re(k_x)$ and $\Im(k_x)$ for the same MoS₂ layer thicknesses are shown in Figure 4g,h. Notably, previous works^{40–42} have already discussed the possibility that the presence of a strongly coupled resonance (the MoS₂ TO phonon, in our case) in the spectral region of the propagating polariton introduces a back-bending in the real part of k_x . The back-bending can hence be interpreted as a signature of strong coupling⁴³ (Figure 4g). This feature starts becoming prominent at $d_{\text{MoS}_2} = 8$ nm and corresponds to an increase in oscillator strength, accompanied by a peak in the propagation losses, as can be seen in Figure 4h. Furthermore, when the in-plane wave vector is plotted in the complex plane in Figure 4e, the curves take on a looping shape at the strong coupling transition, reminiscent of the loops observed using the ellipsometry method (see Figure 4c).

Both methods analyzed in this section are suitable for the study of coupled systems and provide a qualitative criterion for strong coupling between independent material resonances (see SI, section S5 for the study of the two approaches in the context of light–matter coupling). The near-field approach has been experimentally demonstrated^{40,41} using interferometric near-field imaging techniques capable of resolving the complex-valued polariton momentum separately for each real frequency. On the other hand, polariton spectroscopy techniques, such as the prism coupling, typically probe the complex polariton frequency through their finite line width for a given real wave vector, and the dispersion they can map does not feature backbending.²¹ This makes polariton spectroscopy techniques incompatible with and complementary to complex momentum analysis. However, the detection of strong coupling with polariton spectroscopy is possible, but requires careful quantitative spectral analysis of the peak splitting and line widths across the avoided crossing region of the dispersion.²¹ This constraint is removed in the ellipsometry approach presented here. In fact, the loop is a unique signature of strong coupling, provided by the complex representation of ρ . It is contained in each spectrum (at different incidence angles) along the dispersion, only varying in magnitude but not in its topology; see SI, section S8 for a detailed analysis. Furthermore, this secondary loop always emerges at the frequency corresponding to the weak phonon mode of MoS₂ (384 cm⁻¹). In general, the representation of the parameter ρ provided by spectroscopic ellipsometry, as introduced here, opens new avenues for detecting vibrational strong coupling also with far-field spectroscopic techniques.

CONCLUSIONS

In summary, in this work, we demonstrated a new method for retrieving amplitude and phase information for surface phonon polaritons by combining the Otto-type prism coupling technique with spectroscopic ellipsometry. By varying the air

gap width between the prism and the GaP sample, we systematically investigated the behavior of the ellipsometry parameters upon varying the optical coupling efficiency. Analyzing the complex quantity ρ as extracted from the ellipsometry parameters provides new insight into the critical coupling behavior, showing a continuously increasing loop radius when moving from the undercoupled to the overcoupled regime, crossing the origin of the complex plane at critical coupling. To gain a deeper understanding of these circular trajectories in the complex plane, we theoretically compared the evanescent excitation via the prism coupling geometry with free-space excitation with varying oscillator strength of the underlying phonon resonance. Finally, we theoretically studied the feasibility of using surface phonon polariton ellipsometry to characterize vibrational strong coupling. We observed the transition from weak to strong coupling for MoS₂ ultrathin films on GaP through the emergence of a secondary loop in ρ with increasing thickness of the MoS₂. Therefore, polariton ellipsometry and, in particular, complex plane visualization of ρ presents a compelling opportunity by providing a qualitative, topology-based criterion for identifying vibrational strong coupling. More generally, this work demonstrates surface phonon polariton ellipsometry as a powerful tool for the characterization of SPhPs and the analysis of light–matter coupling of materials.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsp Photonics.4c01790>.

Experimental raw data and TM simulations of reflectance spectra; Simulation of ellipsometry parameters: comparison between different methods; Theoretical models of phonon polaritons; Complex-plane versus Poincaré sphere representation; Comparison between methods to identify strong light–matter coupling; A physical explanation for the change in handedness; Transition from weak to strong coupling in the MoS₂ thickness dependence; Formation of complex plane loops in the vicinity of the avoided crossing (PDF)

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■ REFERENCES

- (1) Maier, S. A.; et al. *Plasmonics: fundamentals and applications*; Springer, 2007; Vol. 1.
- (2) Caldwell, J. D.; et al. Low-loss, infrared and terahertz nanophotonics using surface phonon polaritons. *Nanophotonics* **2015**, *4*, 44–68.
- (3) Caldwell, J. D.; et al. Low-loss, extreme subdiffraction photon confinement via silicon carbide localized surface phonon polariton resonators. *Nano Lett.* **2013**, *13*, 3690–3697.
- (4) Khurgin, J. B. Relative merits of phononics vs. plasmonics: the energy balance approach. *Nanophotonics* **2018**, *7*, 305–316.
- (5) Passler, N. C.; et al. Hyperbolic shear polaritons in low-symmetry crystals. *Nature* **2022**, *602*, 595–600.
- (6) Ni, X.; Carini, G.; Ma, W.; Renzi, E. M.; Galiffi, E.; Wassertho, S.; Wolf, M.; Li, P.; Paarmann, A.; Alu, A. Observation of directional leaky polaritons at anisotropic crystal interfaces. *Nat. Commun.* **2023**, *14*, 2845.
- (7) Galiffi, E.; et al. Extreme light confinement and control in low-symmetry phonon-polaritonic crystals. *Nature Reviews Materials* **2024**, *9*, 9–28.
- (8) Gubbin, C. R.; De Liberato, S.; Folland, T. G. Surface phonon polaritons for infrared optoelectronics. *Journal of applied physics* **2022**, *131*, 030901.
- (9) Falge, H.; Otto, A. Dispersion of Phonon-Like Surface Polaritons on α -Quartz Observed by Attenuated Total Reflection. *physica status solidi (b)* **1973**, *56*, 523–534.
- (10) Huber, A.; Ocelic, N.; Kazantsev, D.; Hillenbrand, R. Near-field imaging of mid-infrared surface phonon polariton propagation. *Applied physics letters* **2005**, *87*, 081103.
- (11) Neuner, B., III; et al. Critically coupled surface phonon-polariton excitation in silicon carbide. *Optics letters* **2009**, *34*, 2667–2669.
- (12) Mueller, N. S.; et al. Deep strong light-matter coupling in plasmonic nanoparticle crystals. *Nature* **2020**, *583*, 780–784.
- (13) Barra-Burillo, M.; Muniain, U.; Catalano, S.; Autore, M.; Casanova, F.; Hueso, L. E.; Aizpurua, J.; Esteban, R.; Hillenbrand, R. Microcavity phonon polaritons from the weak to the ultrastrong phonon–photon coupling regime. *Nat. Commun.* **2021**, *12*, 6206.
- (14) Frisk Kockum, A.; Miranowicz, A.; De Liberato, S.; Savasta, S.; Nori, F. Ultrastrong coupling between light and matter. *Nature Reviews Physics* **2019**, *1*, 19–40.
- (15) Thomas, P. A.; Tan, W. J.; Fernandez, H. A.; Barnes, W. L. A new signature for strong light-matter coupling using spectroscopic ellipsometry. *Nano Lett.* **2020**, *20*, 6412–6419.
- (16) Giles, A. J.; et al. Ultralow-loss polaritons in isotopically pure boron nitride. *Nature materials* **2018**, *17*, 134–139.
- (17) Matson, J. R.; Alam, M. N.; Varnavides, G.; Sohr, P.; Knight, S.; Darakchieva, V.; Stokey, M.; Schubert, M.; Said, A.; Beechem, T.; Narang, P.; Law, S.; Caldwell, J. D. The Role of Optical Phonon Confinement in the Infrared Dielectric Response of iii-v Superlattices. *Adv. Mater.* **2024**, *36*, 2305106.

- (18) Ratchford, D. C.; et al. Controlling the infrared dielectric function through atomic-scale heterostructures. *ACS Nano* **2019**, *13*, 6730–6741.
- (19) Chen, M.; Zhong, Y.; Harris, E.; Li, J.; Zheng, Z.; Chen, H.; Wu, J.-S.; Jarillo-Herrero, P.; Ma, Q.; Edgar, J. H.; Lin, X.; Dai, S. Van der Waals isotope heterostructures for engineering phonon polariton dispersions. *Nat. Commun.* **2023**, *14*, 4782.
- (20) Passler, N. C.; et al. Second-harmonic generation from critically coupled surface phonon polaritons. *ACS Photonics* **2017**, *4*, 1048–1053.
- (21) Passler, N. C.; et al. Strong coupling of epsilon-near-zero phonon polaritons in polar dielectric heterostructures. *Nano Lett.* **2018**, *18*, 4285–4292.
- (22) Rønnerstrom, E. L.; et al. Polaritonic hybrid-epsilon-near-zero modes: beating the plasmonic confinement vs propagation-length trade-off with doped cadmium oxide bilayers. *Nano Lett.* **2019**, *19*, 948–957.
- (23) Folland, T. G.; et al. Vibrational coupling to epsilon-near-zero waveguide modes. *ACS Photonics* **2020**, *7*, 614–621.
- (24) Kohlmann, M.; Denker, C.; Passler, N. C.; Kredl, J.; Wolf, M.; Munzenberg, M.; Paarmann, A. Second harmonic generation from grating-coupled hybrid plasmon–phonon polaritons. *Appl. Phys. Lett.* **2022**, *121*, 191105.
- (25) Otto, A. Excitation of nonradiative surface plasma waves in silver by the method of frustrated total reflection. *Zeitschrift für Physik A Hadrons and nuclei* **1968**, *216*, 398–410.
- (26) Schubert, M.; et al. Anisotropy, phonon modes, and free charge carrier parameters in monoclinic β -gallium oxide single crystals. *Phys. Rev. B* **2016**, *93*, 125209.
- (27) Streyer, W.; Law, S.; Rosenberg, A.; Roberts, C.; Podolskiy, V. A.; Hoffman, A. J.; Wasserman, D. Engineering absorption and blackbody radiation in the far-infrared with surface phonon polaritons on gallium phosphide. *Appl. Phys. Lett.* **2014**, *104*, 131105.
- (28) Pufahl, K.; Passler, N. C.; Grosse, N. B.; Wolf, M.; Woggon, U.; Paarmann, A. Controlling nanoscale air-gaps for critically coupled surface polaritons by means of non-invasive white-light interferometry. *Appl. Phys. Lett.* **2018**, *113*, 161103.
- (29) Schöllkopf, W. et al. The new IR and THz FEL facility at the Fritz Haber Institute in Berlin. *Advances in X-ray Free-Electron Lasers Instrumentation III*; SPIE, 2015; Vol. 9512, pp 238–250.
- (30) Zayats, A. V.; Smolyaninov, I. I.; Maradudin, A. A. Nano-optics of surface plasmon polaritons. *Physics reports* **2005**, *408*, 131–314.
- (31) Fujiwara, H. *Spectroscopic ellipsometry: principles and applications*; John Wiley & Sons, 2007.
- (32) Passler, N. C.; Paarmann, A. Generalized 4×4 matrix formalism for light propagation in anisotropic stratified media: study of surface phonon polaritons in polar dielectric heterostructures. *JOSA B* **2017**, *34*, 2128–2139.
- (33) Ashkenov, N.; et al. Infrared dielectric functions and phonon modes of high-quality ZnO films. *J. Appl. Phys.* **2003**, *93*, 126–133.
- (34) Schubert, M.; Tiwald, T.; Herzinger, C. Infrared dielectric anisotropy and phonon modes of sapphire. *Phys. Rev. B* **2000**, *61*, 8187.
- (35) Qin, W.; Kockum, A. F.; Muñoz, C. S.; Miranowicz, A.; Nori, F. Quantum amplification and simulation of strong and ultrastrong coupling of light and matter. *Phys. Rep.* **2024**, *1078*, 1–59.
- (36) Jurna, M.; et al. Visualizing resonances in the complex plane with vibrational phase contrast coherent anti-Stokes Raman scattering. *Analytical chemistry* **2010**, *82*, 7656–7659.
- (37) Autore, M.; et al. Boron nitride nanoresonators for phonon-enhanced molecular vibrational spectroscopy at the strong coupling limit. *Light: Science & Applications* **2018**, *7*, 17172–17172.
- (38) Dolado, I.; Maciel-Escudero, C.; Nikulina, E.; Modin, E.; Calavalle, F.; Chen, S.; Bylinkin, A.; Alfaro-Mozaz, F. J.; Li, J.; Edgar, J. H.; Casanova, F.; Velez, S.; Hueso, L. E.; Esteban, R.; Aizpurua, J.; Hillenbrand, R. Remote near-field spectroscopy of vibrational strong coupling between organic molecules and phononic nanoresonators. *Nat. Commun.* **2022**, *13*, 6850.
- (39) Wieting, T.; Verble, J. Infrared and Raman studies of long-wavelength optical phonons in hexagonal MoS₂. *Phys. Rev. B* **1971**, *3*, 4286.
- (40) Kusch, P.; Mueller, N. S.; Hartmann, M. T.; Reich, S. Strong light-matter coupling in MoS₂. *Phys. Rev. B* **2021**, *103*, 235409.
- (41) Bylinkin, A.; et al. Real-space observation of vibrational strong coupling between propagating phonon polaritons and organic molecules. *Nat. Photonics* **2021**, *15*, 197–202.
- (42) Törmä, P.; Barnes, W. L. Strong coupling between surface plasmon polaritons and emitters: a review. *Rep. Prog. Phys.* **2015**, *78*, 013901.
- (43) Wolff, C.; Busch, K.; Mortensen, N. A. Modal expansions in periodic photonic systems with material loss and dispersion. *Phys. Rev. B* **2018**, *97*, 104203.