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Coherent scattering of exciton polaritons and acoustic phonons in a ZnO single crystal

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The light reflection oscillations resulting from the coherent scattering of polariton states and propagating coherent acoustic phonons (CAPs) in a ZnO single crystal are studied by using a two-color femtosecond pump-probe technique. The oscillation frequency manifested in the photoinduced reflectance shows a nonlinear dependence on the probe-beam wave vector owing to the variation of the refractive index near the band gap. The oscillation amplitude is affected by the refractive index modulation derived from the CAP-detuning polariton states. The larger oscillation for shorter probe-beam wavelengths is consistent with the stronger scattering between the CAP and excitonlike polariton states closer to the band gap.

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Exciton polaritons, quasiparticles resulting from the strong coupling of excitons and photons [1], usually strongly interact with each other and their surrounding media through their excitonic component [2]. Polariton-polariton scattering is the driving force behind various polaritonic nonlinear processes [3,4]. Polaritons can be scattered or modulated by phonons [5], and this leads to the transition between the polariton states on their dispersion [6,7]. In fact, polariton acoustic-phonon (AP) scattering is an effective mechanism for the momentum modulation of polariton [8], especially when the scattering processes are coherent, i.e., polaritons are scattered by specific APs with a given momentum but preserve the phase coherence. It is essential to realize coherent control or modulation of propagating polariton waves for optophononic device applications [9,10]. However, due to the small change of energy and the relatively weak interaction strength compared with other polaritonic scatterings, the coherent scattering of polariton and AP is yet to be demonstrated.

With the fast development of femtosecond and picosecond lasers, coherent acoustic-phonon (CAP) waves could be effectively generated in semiconductors, metallic films, and some other heterostructures by optical excitation [11–15]. Due to the interaction of the CAP and the electronic or excitonic states, the refractive index and the reflectivity of the materials are modulated. Using the optical pump-probe technique, the scattering of the CAP manifests itself as periodic oscillations in the time-resolved reflectance of the probe light [16]. However, most of the previous experiments on the CAP scatterings are performed with the probe photon energy far below the band-gap energy (and/or the excitonic energies) to avoid light absorption by the materials [14]. As a result, how the CAP waves affect the reflectivity by modulating the electronic structures near critical energies such as the band edges [17], excitonic [18,19], and, most importantly, the polaritonic states, i.e., the scattering characteristic of the CAP and polariton, remains unexplored.

In this Rapid Communication, we demonstrate the CAP scattering of the polariton states in semiconductors: A two-color femtosecond pump-probe reflectivity measurement is adopted to generate and detect the CAP in a typical metal-semiconductor heterostructure sample, i.e., ZnO coated with a thin Au film. The heat-induced lattice expansion in the Au film after absorbing the pump laser pulse generates CAP waves transmitting into the ZnO sample, and then the CAP waves modulate the polariton states. For different probe-light wavelengths, the modulation strength of the polariton states which manifests itself by the changes of the refractive index is extracted from the amplitude of the probe-light reflectance, and compared with the theory of polariton-CAP scattering.

The sample we used is a 0.5-mm-thick ZnO single crystal (wurtzite structure, c plane) with an 8-nm-thick Au film deposited on the top by using the magnetron sputtering technique. The coated Au film facilitates the enhancement of the thermal-induced CAP wave [20]. The pump-probe measurements are performed by using a mode-locked Ti:sapphire femtosecond laser with a pulse width of $\sim$100 fs, and a repetition rate of 80 MHz. The output laser beam is divided by a beam splitter into the pump and probe light. The pump light passes an acoustic optical modulator with a modulation frequency of 50 kHz, and then is normally incident on the sample with a spot diameter of $\sim$150 μm, and energy density of $\sim$12 μJ/cm^2. A beta barium borate crystal is used to generate the frequency-doubled ultraviolet light as the probe light, which is incident at an angle of 40° with a p-polarization configuration on the sample as shown in Fig. 1(a), and the spot size is slightly smaller than the pump spot. The weak modulation of the reflected probe light is measured by a lock-in amplifier combined with a sensitive photodetector. A variable optical delay line is placed in the probe-beam path to vary the time delay (τ) between the pump and probe pulses. In order to tune the probe-light wavelength near the ZnO band-gap energy ($\sim$3.3 eV), the corresponding pump wavelengths vary within 750–800 nm (well below the band-gap energy). However, the absorption of Au in such a wavelength range keeps almost constant, so the heating effect and the resultant CAP wave do not change [21].

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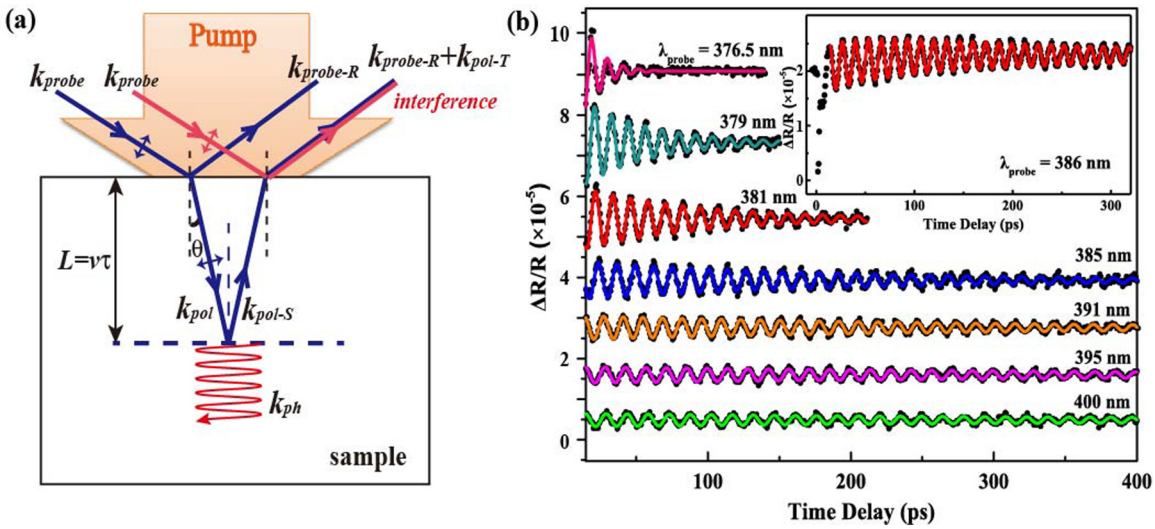

FIG. 1. (Color online) (a) The schematic diagram of the coherent scattering process between the polariton wave and AP wave at a fixed delay time τ. (b) The oscillatory components of the $\Delta R/R$ signals for different probe-light wavelengths from the ZnO single crystal coated with 8-nm-thick Au film, as functions of the pump-probe delay time. The inset shows the transient reflection signal with a sharp change immediately following pump excitation for probe wavelengths of 386 nm.

In the presence of CAP, the reflectivity R of the sample is modulated. As a result, the time evolution of transient differential reflectivity $\Delta R/R$ signals displays periodic oscillations with respect to τ, as shown in Fig. 1(b). The period and amplitude of $\Delta R/R$ display a strong variation for different probe-light wavelengths. Phenomenologically, the modulated ΔR can be regarded as the self-interference between two probe reflections, one from the sample surface and the other from the CAP wave [22], as schematically shown in Fig. 1(a). When the probe pulse reaches the sample surface at τ after the pump pulse, the CAP wave induced by the pump pulse has propagated a distance $L = v\tau$, with v being the sound velocity along the $\boldsymbol{c}$-axis direction in ZnO. The amplitude $\xi_{\rm ph}$ of the phonon wave has weakened as $\xi_{\rm ph} = \xi^0_{\rm ph} e^{-\alpha_{\rm ph} L}$, where $\xi^0_{\rm ph}$ is the initial amplitude, and $\alpha_{\rm ph}$ is the absorption coefficient of the phonon in ZnO. Considering that the velocity of the polariton is orders of magnitude larger than the sound velocity, the polariton wave in ZnO will propagate the distance $L/\cos\theta$ with a much shorter time and be scattered by the AP wave. Due to the requirement of momentum conservation in the polariton-AP scattering processes, only those APs with a specific momentum $\mathbf{k}_{\rm ph} = \mathbf{k}_{\rm pol} - \mathbf{k}_{{\rm pol}-S}$ can scatter strongly with the polariton wave, where $\mathbf{k}_{\rm pol}$ and $\mathbf{k}_{{\rm pol}-S}$ are the momenta of the polariton before and after scattering. Because of the very thin thickness of the Au film, the CAP momentum width is much larger than $\mathbf{k}_{\rm pol}$. In addition, as the energy of AP is much smaller than that of a polariton, the scattering is in fact a Brillouin scattering process, with the energy shift of the polaritons being small. Thus, $|\mathbf{k}_{\rm pol}| \approx |\mathbf{k}_{{\rm pol}-S}|$ and the momentum change of the polariton can be obtained as $\Delta\mathbf{k}_{\rm pol} = \mathbf{k}_{\rm ph} \approx 2|\mathbf{k}_{\rm pol}|\cos\theta \times \mathbf{e}_{\rm ph}$. Meanwhile, the scattering angle is nearly twice the probe-light refraction angle θ. The amplitude of the scattered polariton wave $\xi_{{\rm pol}-S}$ can thus be described as [23] $\xi_{{\rm pol}-S} \propto S_C(\lambda)\xi_{\rm pol}\xi_{\rm ph} = S_C(\lambda)\xi^0_{\rm ph}\xi^0_{\rm pol} e^{-(\alpha_{\rm ph}L + \alpha_{\rm pol}L/\cos\theta)}$, where $S_C(\lambda)$ is the scattering coefficient for the probe-beam wavelength λ, $\xi^0_{\rm pol}$ is the amplitude of the probe light transmitted into ZnO, and $\alpha_{\rm pol}$ is the absorption coefficient of the polariton wave. The scattered polariton wave propagates towards to the sample surface, refracts out, and interferes with the probe light reflected directly at the sample surface. Thus, the modulated reflectivity $\Delta R/R$ can be expressed as [11,24]

$$\frac{\Delta R(\tau)}{R} \propto S_C(\lambda) e^{-\tau/T} \sin(2\pi f\tau + \varphi), \tag{1}$$

$$f\tau = 2L\frac{n(\lambda)\cos\theta}{\lambda} = \frac{v\tau}{\pi}|\mathbf{k}_{\rm probe}|n(\lambda)\cos\theta, \tag{2}$$

$$T = \frac{1}{v}\left(\alpha_{\rm ph} + \frac{2\alpha_{\rm pol}}{\cos\theta}\right)^{-1}, \tag{3}$$

where $\mathbf{k}_{\rm probe}$ is the probe-beam wave vector, f is the oscillation frequency of the $\Delta R/R$ signals, φ denotes the phase shift, and $n(\lambda)$ represents the refractive index of ZnO. Due to the coherent scattering of polaritons and APs, the phases of scattered polaritons are preserved and the superposition of the reflective signals results in the interference oscillation as a function of τ. The exponential term in Eq. (1) describes the amplitude decay of the polariton wave scattered by the AP.

The solid curves in Fig. 1(b) are the fitting results given by Eq. (1). One can see that the fitting curves match well with the experiment results (the black dots). Besides the coherent oscillations discussed above, a rapid change in the transient reflectance signal within the initial 3 ps is observed, as illustrated in the inset of Fig. 1(b). This is mainly caused by the nonequilibrium dynamics of photoexcited carriers in the metal film [25]. Here we focus on the coherent process with a longer duration [26].

The oscillation frequency f extracted from the fitting shown in Fig. 2(a) displays a strong nonlinear dependence on $\mathbf{k}_{\rm probe}$. From Eq. (2), one can see that f for the specific probe wavelength is equal to the frequency of the scattered AP ($f_{\rm ph}$)

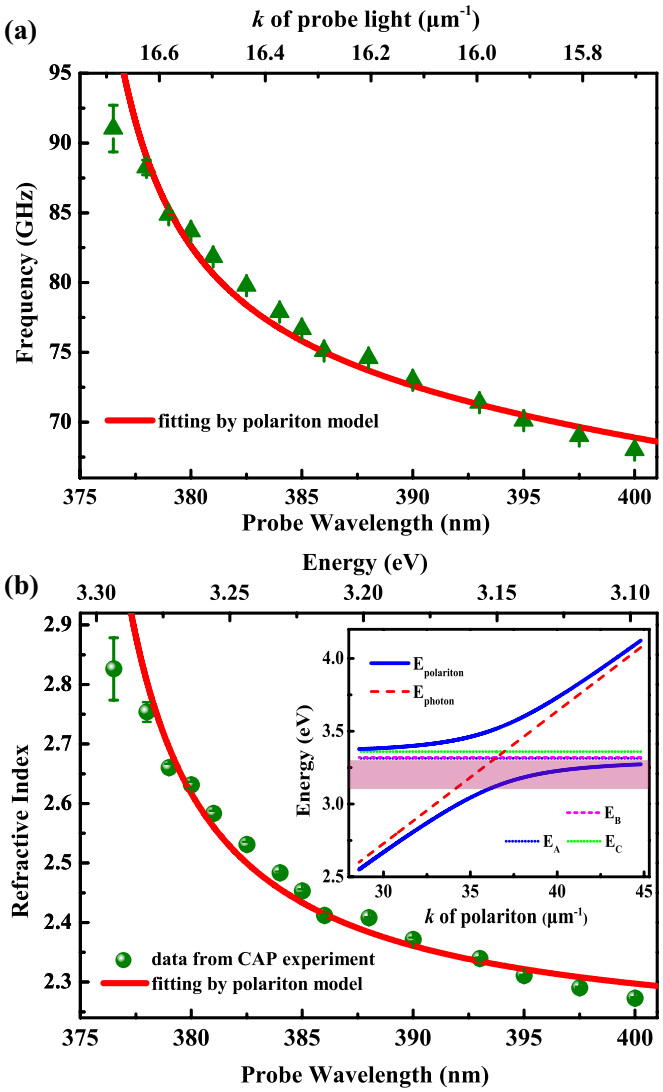

FIG. 2. (Color online) (a) The probe-beam wavelength dependence of the oscillation frequency of the $\Delta R/R$ signals (solid triangles). (b) The refractive index vs the probe-beam wavelength; the inset shows the calculated exciton-polariton dispersion.

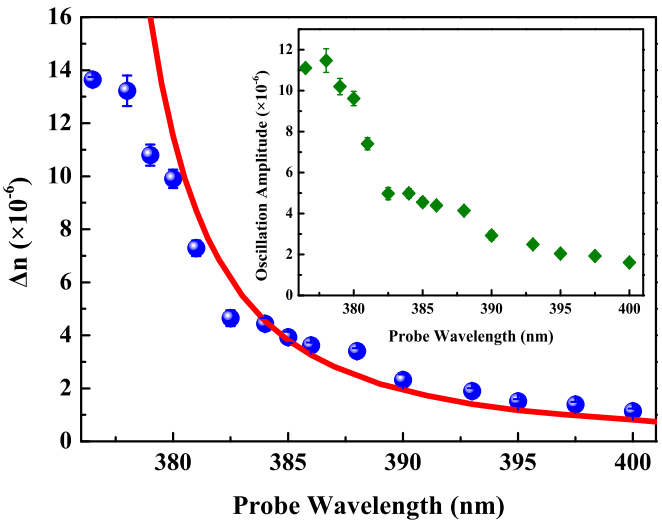

FIG. 3. (Color online) The Δn induced by the polariton-CAP scattering. The inset shows the probe-light wavelength dependence of the oscillation amplitude of the $\Delta R/R$ signals.

with the corresponding momentum, because $f_{\rm ph} = \frac{v}{2\pi}|\mathbf{k}_{\rm ph}| = \frac{v}{\pi}|\mathbf{k}_{\rm probe}|n(\lambda)\cos\theta$. Therefore, such results also indicate a nonlinear relationship between the scattered AP frequency and $\mathbf{k}_{\rm probe}$. This is different from the linear $f_{\rm ph} - \mathbf{k}_{\rm probe}$ dependency in the previous reports in which the probe phonon energy is well below the band-gap energy [14,16]. The rapid increase of the AP frequency at the near-band-gap energy mainly originates from the variation of the momentum $|\mathbf{k}_{\rm pol}|$, as described by the scattering momentum-change equation of the polariton, i.e., the nonlinear dispersion of polariton [27–29]. When the probe light propagates in the sample, it will strongly couple with the excitons and behave as exciton-polariton wave with a nonlinear dispersion [30,31], contributing significantly to the variation of the refractive index near the band gap. In order to compare the refractive index obtained from the experiments and the polariton model, we deduce $n(\lambda)$ from the AP frequency data with Eq. (2) using a sound velocity of 6200 m/s [32]. The results are shown as the solid circles in Fig. 2(b). We use the exciton-photon coupling model (see the Supplemental Material) to fit f and $n(\lambda)$ [33]. Due to the large incident angle of the probe beam, the reflective index comes from the transverse magnetic ($E \parallel c$) polarized polariton modes, and all the A, B, and C excitons contribute to the nonlinear exciton-polariton dispersion [29], but the coupling of the photon and A, B excitons plays a much more important role [34,35]. The fitting results are shown as solid curves in Figs. 2(a) and 2(b). The inset of Fig. 2(b) is the exciton-polariton dispersion, derived from the polariton model with the fitting parameters in the Supplemental Material [33].

In the following, we will discuss the oscillation amplitude which reflects the scattering coefficient $S_C(\lambda)$. The scattering strength is correlated with the CAP detuning of the polariton states which, on the other hand, determine the refractive index modulation Δn. Thus, the CAP oscillation can also be simulated with the interference model by considering the reflectivity change due to Δn using Fresnel equations. It turns out that such a model leads to the same frequency formula as in Eq. (2). In addition, we may extract Δn from the oscillation amplitude, and compare to that derived from the detuning of the polariton states.

The solid circles in Fig. 3 represent the probe-light wavelength dependent Δn extracted from the measured oscillation amplitude (the inset of Fig. 3). We also deduce the $\Delta n - \lambda$ relationship from the polariton-phonon coupling model. In such a model, an energy change of the exciton in the polariton ΔE_X is introduced by the lattice distortion due to the CAP. For the polariton state with a certain energy, its momentum has a correspondent variation $\Delta k_{LP}(\lambda) = \Delta E_X(\frac{\partial k_{LP}}{\partial E_X})_{E_{LP}=hc/\lambda}$. Thus, Δn can be obtained as $\Delta n(\lambda) = \frac{\hbar c}{E_{LP}}\Delta k_{LP}(\lambda)$. With $\Delta E_X = 1.6\ \mu$eV, we calculate Δn for different probe-beam wavelengths, shown as a solid curve in Fig. 3. The calculated Δn agrees well with that obtained from the measured oscillation amplitude. This result thus corroborates the scattering model of CAP and polariton states near the band gap. In particular, the scattering strength becomes stronger for

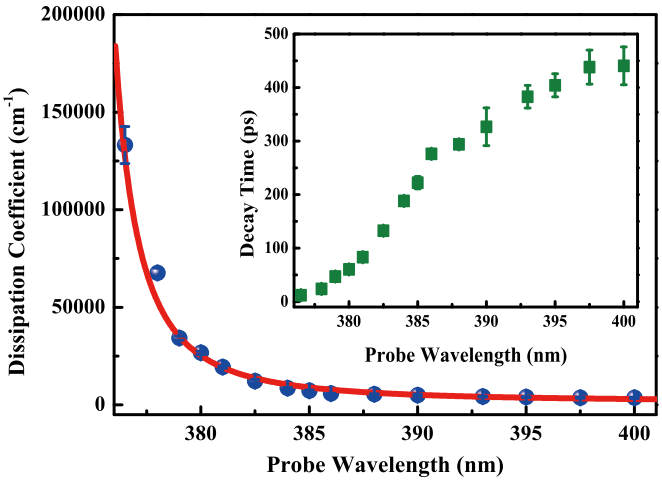

FIG. 4. (Color online) The dissipation coefficient of the polariton waves in the sample near the band gap of ZnO. The inset shows the time decay of the $\Delta R/R$ oscillations.

excitonlike polaritons than the photonlike polaritons [33], as the oscillation amplitude and Δn increase for probe-light energies closer to the band gap.

Apart from the significant variation of the oscillation amplitude, we also note from Fig. 1(b) that the oscillation decay becomes much more rapid for probe energies closer to the band gap. From the fitting of the oscillations by Eq. (1), we obtain the decay time T shown in the inset of Fig. 4. The decay of the oscillations is associated with the attenuation of both the polariton and phonon waves, as described by Eq. (3). The decay is relatively slower at the longer probe wavelengths, because the exciton component of the polariton wave is relatively small and it is not easy to dissipate during the propagation. In this case, the dissipation of the phonon wave is the main contribution to T. With the probe-light wavelength approaching 375 nm, the increased exciton components lead the polariton wave to dissipate within ~10 ps, where T is mainly determined by the dissipation of polariton waves. Therefore, we calculate the dissipation coefficient of the scattering oscillation amplitude $D(\lambda) = (vT)^{-1}$, shown as solid circles in Fig. 4. The thus obtained $D(\lambda)$ can be well fitted (solid curve in Fig. 4) by $D(\lambda) = \alpha_{\rm ph} + \frac{2\alpha_{\rm pol}}{\cos\theta}$ from Eq. (3). Here, we use the fitting parameters $\alpha_{\rm pol}$ from Refs. [30,36], and $\alpha_{\rm ph} = 1610\ {\rm cm}^{-1}$ corresponding to the AP lifetime of ~1 ns. In order to verify that the oscillation decay and frequency are independent on the pump power and the amplitude is in the linear response regime, we vary the pump power in the measurements, and the results are discussed in the Supplemental Material [33].

In conclusion, we observe light reflection oscillations caused by the interaction of propagating CAP and polariton states in a bulk ZnO single crystal by a two-color femtosecond pump-probe technique. We reveal a nonlinear relationship of the oscillation frequency with the probe-beam wave vector near the band gap owing to the variation of the refractive index. The oscillation amplitude is effectively accounted by the index refraction modulation derived from the CAP detuning of the polariton states. The larger oscillation for the shorter probe wavelength is consistent with the stronger interaction between the CAP and the excitonlike polariton states closer to the band gap. Our results show a potential application for developing the acoustic-phonon modulated polariton devices.

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