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Coherent optical phonons of ZnO under near resonant photoexcitation

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Abstract

Ultrafast electron–phonon coupling dynamics in ZnO are investigated by degenerate pump–probe reflectivity measurements using near resonant 400 nm light. Because of the below-gap excitation, photocarriers are excited primarily from deep levels of intrinsic point defects. At least six coherent phonon modes, including two E2 modes and their combination, longitudinal optical (LO) mode and its overtone (2LO), are observed. Unlike the previous resonant Raman studies using 325 nm light, the intensity of the polar LO phonons is only moderately enhanced by the Fröhlich interaction. The non-polar E2 phonons decay considerably faster than under visible excitation, indicative of strong deformation potential interaction with photocarriers. The overdamped oscillation centered at around 20 THz is tentatively attributed to the upper branch of the plasmon–phonon coupled mode. The pump-polarization dependence of the phonon amplitudes is consistent with the impulsive Raman generation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

A wide band gap semiconductor, ZnO, has attracted much attention as a material for optoelectronic, spintronic, sensor, and catalytic applications [1, 2]. ZnO has a direct gap of 3.3 eV at room temperature and a large exciton binding energy of 60 meV, making it a promising candidate for ultraviolet (UV) light-emitting-diodes and lasers. For many of these applications, the carrier-density dependent electron–phonon interaction can significantly impact the optical and electronic properties of ZnO.

Lattice dynamics have been studied extensively by Raman scattering. The optical phonon modes of wurtzite ZnO include the Raman-and-infrared active A1 and E1, the Raman active E2, and the silent B1. While the phonon peaks appear according to the symmetry selection rules in the non-resonant Raman spectrum [3–6], under resonant UV excitation the polar LO phonon peaks and their overtones are enhanced to such an extent that they dominate the Raman spectra even in the symmetry-forbidden configurations [5, 7–9]. Such ‘dipole-forbidden’ LO scattering arises from the intraband Fröhlich scattering with finite scattering vectors (q ≠ 0). The finite value of q raises the minimum gap for valence-conduction transitions to ω0(q) ≈ ω0 + q2/2me and ω0 + q2/2mh for conduction and valence intraband scattering, respectively. The contribution of the two q-dependent gaps to the Raman susceptibility does not cancel out, but a term proportional to q remains as a difference [10].

Electron–phonon interaction has been one of the important subjects of the Raman studies, because it defines the carrier lifetimes as well as transport properties of ionic crystals. In the case of ZnO, in which long-range electrostatic forces dominate over the anisotropy in the short-range forces, mixing occurs between the A1- and E1-symmetry LO (or TO) phonons when they propagate along a direction between the x and z axes. The frequency of these ‘quasi-LO (or TO)’ phonons is determined by the angle of the phonon propagation, and therefore by the angle of incidence of the excitation light,
relative to the crystalline high-symmetry axes [5, 11, 12]. Long-range electrostatic field also leads to the emergence of the LO phonon–plasmon coupled (LOPC) modes through the interaction between the lattice vibration and the electronic polarization [13]. Though the frequencies of the LOPC modes follow the well-known dispersion relation in an isotropic polar crystal [14], little has been established for a uniaxial crystal like wurtzite ZnO [15].

Time-domain observation of coherent phonons can give insight complementary to the frequency-domain vibrational spectroscopy. Beside the accurate determination of phonon lifetimes, coherent phonon spectroscopy also has potential to reveal the time-evolution of electron–phonon coupling under non-equilibrium carrier generation [16, 17]. For ZnO, high- and low-frequency E2 modes at 444 and 99 cm\(^{-1}\) have been observed as the coherent modulation of transmissivity under near-infrared (NIR) excitation [18, 19], as expected for the Raman selection rules in the backreflection from the c-plane. At room temperature, the dephasing times are measured to be 1.75 and 29.2 ps for the high- and low-frequency E2 modes [18], while at 5 K, the coherent low-E2 mode was found to have an exceptionally long decay time of 210 ps, corresponding to a linewidth of 0.05 cm\(^{-1}\) [19].

In the present study we examine the ultrafast electron–phonon coupling in ZnO using sub-10 fs pulses at 3.1 eV. Time-resolved reflectivity shows an exponential recovery within \(\sim 1\) ps, which is indicative of the excitation of carriers via the deep defect levels. Multi-mode coherent oscillation is superimposed on the exponential recovery. With time-windowed Fourier-transformed (FT) analyses we reveal the ultrafast formation of six phonon modes and possibly the plasmon–phonon hybrid mode out of the high-density electron–hole plasma. Time-domain analyses of the oscillation demonstrate that the coherent phonons couple with photoexcited carriers via the deformation potential or the Fröhlich interactions under the near resonant excitation.

2. Experimental details

The sample studied was a wurtzite ZnO film grown by pulsed laser deposition (PLD) on Al\(_2\)O\(_3\) (1120) substrate. Details of the sample preparation and evaluation are described elsewhere [20]. In short, we employed a four-step PLD process to grow a high-quality ZnO film on an Al\(_2\)O\(_3\) substrate using a ZnO interlayer grown at reduced temperature. The lattice constant obtained from a high-resolution x-ray diffraction measurement suggested that the ZnO epitaxial layer was close to a strain-free monocrystal. Atomic force microscope images showed a large lateral grain size of \(0.25-0.5\ \mu\text{m}\) for a \(2\ \mu\text{m}\) thick film. Hall effect measurements showed a residual carrier concentration of \(\sim 1 \times 10^{16} \text{cm}^{-3}\) and a mobility of \(\sim 100\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}\). Low-temperature photoluminescence from the film was dominated by the recombination of bound excitons at 3.361 eV and their LO phonon replicas, while the intensity of deep-level green emission was negligible.

Pump–probe reflectivity measurements were performed using optical pulses with \(<10\ fs\) duration, 400 nm wavelength (3.1 eV energy), and 70 MHz repetition rate. A spherical mirror brought linearly polarized pump and probe beams to a common \(25\ \mu\text{m}^2\) spot on the sample with angles of \(20^\circ\) and \(5^\circ\) from the surface normal, respectively. Spatial overlap of the pump and probe spots on the sample surface was optimized to give the maximum oscillatory signal in the reflectivity. The optimal overlap was confirmed by replacing the ZnO sample with a standard sample such as Si [16]. Pump-induced change in the reflectivity \(\Delta R\) was measured by sampling the probe beam intensity before and after reflection from the sample surface with a pair of matched photodiodes. The difference-signal obtained by subtracting the signals from the two photodiodes was amplified with a pre-amplifier and accumulated in a digital oscilloscope while the time delay between the pump and probe pulses was scanned at a 20 Hz rate. The signal was taken by scanning the delay from the positive to negative delay time, so that any distortion in the electric response of the detection system by the intense coherent artifact at zero delay would not affect the phonon signal. The noise from mechanical and electric sources was minimized by band-pass filtering the signal with the pre-amplifier. The setup enables us to detect the reflectivity change \(\Delta R/R\) smaller than \(10^{-6}\) for opaque [17] and transparent [21] samples with polished surfaces. In the present study, however, the scattering of the pump and probe light by the rough surface of our ZnO sample reduced the signal-to-noise ratio.

Raman scattering measurements were carried out in a 90\(^\circ\)-scattering configuration using 514.5 nm (2.41 eV) light as the excitation source. Nominal wavenumber resolution was \(<1\ cm^{-1}\). The Raman spectrum of our sample looks reasonably similar to the non-resonant Raman spectra from the a-plane of ZnO single crystals [3–5], confirming our sample’s crystalline quality. Both the time-resolved and Raman measurements were carried out at room temperature.

3. Results and discussion

Figure 1 shows the pump-induced reflectivity change \(\Delta R/R\) from the ZnO sample. The reflectivity drops at photoexcitation \((t = 0)\), and recovers within 2 ps with an approximately exponential response. The exponential recovery suggests that light excites real charge carriers in the sample. We expect that the photoexcitation at 3.1 eV occurs through a combination of one and two-photon processes [22]. Since our excitation pulse has a very small spectral component exceeding the band gap, it is likely that one-photon absorption involves the deep levels such as Zn-interstitials at \(E_c-0.22\ \text{eV}\) and Zn-vacancies at \(E_c-0.36\ \text{eV}\) [23], where \(E_c\) denotes the energy of the conduction band minimum. These deep levels contribute to the finite absorption, \(\alpha = 4.7 \times 10^4 \text{cm}^{-1}\), at 3.1 eV for a rather defective ZnO single crystal [24], whereas the absorption is one order of magnitude smaller (\(\alpha \sim 1 \times 10^3 \text{cm}^{-1}\)) for a less defective crystal [25].

Superimposed on the exponential recovery is a small and complex oscillatory response due to coherent phonons. The coherent oscillation in the present study appears very different from that obtained from the c-plane using NIR pulses, which featured the long-lived high- and low-frequency E2 modes at 13 and 3 THz [18, 19]. The FT spectra in figure 2(a) demonstrate...
that the coherent oscillation consists of several components whose frequencies range between 2 and 35 THz. Our FT spectra resemble the resonant Raman spectra excited with UV light [3–9] rather than the non-resonant spectrum at 2.4 eV (figure 2(b)), in that the peaks at 18 and 35 THz (580 and 1150 cm$^{-1}$) are the most distinct. However, the appearance of the broad background and of the LO mode as a negative peak against it makes the decomposition and assignment of the FT peaks challenging in the present study.

To get a better insight into the ultrafast carrier–phonon interactions, we performed a time-windowed Fourier transform analysis of the $\Delta R/R$ signal, to obtain the frequency–time plot shown in figure 3. At early time ($t < 0.3$ ps), we see a broadband response extending up to 35 THz; at later time, several horizontal bands emerge from the broadband response at $\sim$10, 13, 18 and 35 THz, all of which decay within 1 ps. Where the band at $\sim$18 THz crosses the broadband response in time and frequency, we see a dip, corresponding to the negative peak in the FT spectra in figure 2. Based on this analysis, we decomposed the oscillatory part of the $\Delta R/R$ signal into a linear combination of the damped-harmonic functions, as shown in figure 4. The obtained frequencies and dephasing rates are listed in table 1. Good agreement between the experimental data and the fit is demonstrated in the time domain in figure 4(a) and in the frequency domain in figure 2.

The modes at 17.5 and 34.5 THz were assigned as the fundamental and first overtone of the LO mode in previous resonant Raman studies [3–9]. We consider that the coherent phonons in the present study are generated via impulsive stimulated Raman scattering (ISRS) [26], as we will discuss in detail below. Under our excitation at 3.1 eV, we expect the amplitudes of the polar LO and 2LO phonons to be resonantly enhanced by the dipole-forbidden Fröhlich scattering, more significantly than that below 3 eV excitation [4], but not to such an extent that they overwhelm the whole spectrum, as observed at 3.8 eV [5, 7–9]. Strictly speaking, the 17.5 THz frequency (585 cm$^{-1}$ in the Raman spectrum) lies between those of the $E_1(LO)$ and $A_1(LO)$ modes, 17.2 and 17.7 THz [6], respectively, which is indicative of a quasi-LO mode, i.e. mixing of $E_1$- and $A_1$-symmetries due to a finite angle between the phonon propagation and the high-symmetry axes of the crystal. Such quasimodes have previously been
Table 1. Frequency, dephasing rate, and possible assignment of the coherent phonons of ZnO, obtained from fitting of the time-domain oscillation in figure 4. Frequencies obtained from the Raman spectrum in figure 2(b) are also listed.

<table>
<thead>
<tr>
<th>Coherent phonons</th>
<th>Frequency in THz</th>
<th>Dephasing rate in ps⁻¹</th>
<th>Raman</th>
<th>Frequency in THz (cm⁻¹)</th>
<th>Reference</th>
<th>Frequency in cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>~3ᵃ</td>
<td>&gt;5</td>
<td>Raman</td>
<td>9.9³ᵇ</td>
<td>E₂⁺</td>
<td>105³ᵇ</td>
<td>E₂⁻⁺</td>
</tr>
<tr>
<td></td>
<td>9.7 ± 0.3</td>
<td>3.7 ± 2.0</td>
<td>Raman</td>
<td>13.2³ᵇ</td>
<td>E₂⁺</td>
<td>180³ᵇ</td>
<td>E₂⁻⁺</td>
</tr>
<tr>
<td></td>
<td>12.8 ± 0.4</td>
<td>8.1 ± 2.6</td>
<td>Raman</td>
<td>13.2³ᵇ</td>
<td>E₂⁺</td>
<td>180³ᵇ</td>
<td>E₂⁻⁺</td>
</tr>
<tr>
<td></td>
<td>15.9 ± 0.3</td>
<td>3.4 ± 1.8</td>
<td>Raman</td>
<td>17.0³ᵇ</td>
<td>E₂⁺</td>
<td>222³ᵇ</td>
<td>E₂⁻⁺</td>
</tr>
<tr>
<td></td>
<td>17.5 ± 0.1</td>
<td>3.0 ± 0.8</td>
<td>Raman</td>
<td>17.5³ᵇ</td>
<td>E₂⁺</td>
<td>222³ᵇ</td>
<td>E₂⁻⁺</td>
</tr>
<tr>
<td></td>
<td>~20ᵃ</td>
<td>&gt;20</td>
<td>Raman</td>
<td>19 ± 9</td>
<td>E₂⁺</td>
<td>222³ᵇ</td>
<td>E₂⁻⁺</td>
</tr>
<tr>
<td></td>
<td>34.57 ± 0.05</td>
<td>5.0 ± 0.3</td>
<td>Raman</td>
<td>34.5³ᵇ</td>
<td>E₂⁺</td>
<td>222³ᵇ</td>
<td>E₂⁻⁺</td>
</tr>
</tbody>
</table>

ᵃ These oscillations cannot be described as damped-harmonic functions (see figure 4(b)).
ᵇ Reference [6].  The strongly time-dependent frequency and the fast decay, however, suggest a different origin. A possible assignment is to the upper (L⁺) branch of the LOPC mode, which would appear at 20 THz for a carrier density of 5 × 10¹⁸ cm⁻³ [15]. This carrier density

reported in non-resonant [11] and resonant [5] Raman studies on ZnO. If we assume a uniform tilt of the crystalline domains, we can estimate from the observed frequency the angle θ of the c axis to be 50° ± 17° relative to the surface normal.

We assign the coherent modes at 12.8 and 9.7 THz to the high-frequency E₂ mode (E₂⁺) and the difference mode between the two E₂ modes (E₂⁺⁻E₂⁻), respectively [4–6]. These two modes have lower frequencies than their counterparts in the Raman spectrum under visible excitation (13.2 and 10.2 THz, respectively), and decay considerably faster than expected from the Raman linewidths. We attribute the discrepancy to a coupling with photoexcited carriers via the deformation potential. This is plausible, since a previous resonant Raman study estimated relatively large deformation potential coefficients for the E₂⁺⁻E₂⁻ modes based on the photon-energy dependence of the Raman scattering cross section below the direct band gap [4]. The large coupling was explained in terms of the sensitivity of the E₂ mode with respect to observed at >15 THz, which would appear at 20 THz for a carrier density of 5 × 10¹⁸ cm⁻³ [15]. This carrier density.
we found the non-polar $E_2$ modes decayed significantly faster than the amplitude of the polar LO modes by Fröhlich interaction, plasma. While we observed only moderate enhancement in phonon hybrid mode out of the high-density electron–hole formation of six phonon modes and possibly of the plasmon–FT analyses of the reflectivity we revealed the ultrafast deep levels of intrinsic point defects. With time-windowed time, indicative of the photoexcitation of carriers via the excitation. Time-resolved reflectivity had a finite recovery dynamics in wurtzite ZnO film under near resonance the TDFS contribution is small in the present study. than in the non-resonant Raman spectrum, we conclude that be generated via TDFS under resonant excitation. Because the polarization angle of the pump light parallel with (perpendicular to) that of the probe light.

could be achieved with the pump density in the present study $(7 \times 10^{18}–7 \times 10^{19}$ photons cm$^{-3}$) if there is sufficient density-of-states. In the present study, we did not observe the lower ($L^-$) branch of the LOPC mode as a distinct peak. It would appear, if the damping is sufficiently small, at a frequency between those of the $E_2^{\text{high}}–E_2^{\text{low}}$ modes, where our FT spectra have a broad background.

As we have alluded to above, we consider that the coherent phonons are generated via ISRS with 3.1 eV excitation. This is confirmed experimentally by the pump-polarization dependence shown in figure 5; the peak height of the $E_2^{\text{low}}$, $E_2^{\text{high}}–E_2^{\text{low}}$, IFO, and 2LO modes depends critically on the pump polarization, excluding other generation mechanisms such as transient depletion field screening (TDFS) [30]. Only the LO phonon remains comparable in the peak height after varying the pump polarization by 90°, which is consistent with both the ISRS and TDFS generations for a fully symmetric $A_1$(LO) mode. In principle, the polar phonon modes could also be generated via TDFS under resonant excitation. Because the relative peak height of the LO mode is not significantly larger than in the non-resonant Raman spectrum, we conclude that the TDFS contribution is small in the present study.

In summary, we studied coherent electron–phonon dynamics in wurtzite ZnO film under near resonance excitation. Time-resolved reflectivity had a finite recovery time, indicative of the photoexcitation of carriers via the deep levels of intrinsic point defects. With time-windowed FT analyses of the reflectivity we revealed the ultrafast formation of six phonon modes and possibly of the plasmon–phonon hybrid mode out of the high-density electron–hole plasma. While we observed only moderate enhancement in the amplitude of the polar LO modes by Fröhlich interaction, we found the non-polar $E_2$ modes decayed significantly faster compared with the non-resonant visible excitation on account of deformation potential coupling.

Acknowledgment

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