The effect of n- and p-type doping on coherent phonons in GaN

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Abstract
The effect of doping on the carrier–phonon interaction in wurtzite GaN is investigated by pump–probe reflectivity measurements using 3.1 eV light in near resonance with the fundamental band gap of 3.39 eV. Coherent modulations of the reflectivity due to the $E_2$ and $A_{1}$(LO) modes, as well as the $2A_1$(LO) overtone are observed. Doping of acceptor and donor atoms enhances the dephasing of the polar $A_1$(LO) phonon via coupling with plasmons, with the effect of donors being stronger. Doping also enhances the relative amplitude of the coherent $A_1$(LO) phonon with respect to that of the high-frequency $E_2$ phonon, though it does not affect the relative intensity in Raman spectroscopic measurements. We attribute this enhanced coherent amplitude to the transient depletion field screening (TDFS) excitation mechanism, which, in addition to impulsive stimulated Raman scattering (ISRS), contributes to the generation of coherent polar phonons even for sub-band gap excitation. Because the TDFS mechanism requires photoexcitation of carriers, we argue that the interband transition is made possible at a surface with photon energies below the bulk band gap through the Franz–Keldysh effect.

(Some figures may appear in colour only in the online journal)

1. Introduction

Gallium nitride (GaN) is an important optoelectronic semiconductor with a direct-gap of 3.39 eV at room temperature. The optical properties of GaN depend on the rapid exchange of energy between the electronic and the lattice subsystems [1–3]. The wurtzite polymorph of GaN has optical phonon modes of $A_1$ (Raman (R) and infrared (IR) active), $E_1$ (R and IR active), $E_2$ (R active) and $B_1$ (silent) symmetries [4–6], whose atomic displacements are summarized in figure 1. The frequencies of the IR active $A_1$ and $E_1$ modes are split into longitudinal optical (LO) and transverse optical (TO) components by the macroscopic electric field associated with the LO phonon. This electric field stiffens the force constant and thereby increases the LO frequency over the TO. For wurtzite GaN the LO–TO splitting is greater than the $A_1$–$E_1$ splitting, i.e., $|\Omega_{LO}^{(A_1)} - \Omega_{TO}^{(A_1)}|$ and $|\Omega_{LO}^{(E_1)} - \Omega_{TO}^{(E_1)}| \gg |\Omega_{LO}^{(A_1)} - \Omega_{LO}^{(E_1)}|$ and $|\Omega_{TO}^{(A_1)} - \Omega_{TO}^{(E_1)}|$, indicating that the short-range forces are dominated by the electrostatic force rather than the interatomic anisotropy in [7].

Like in zinc-blende crystals, the LO phonons in wurtzite GaN can couple with plasmons to form LO phonon–plasmon coupled (LOPC) mode [4, 8–11]. The $A_1$- and $E_1$-like LOPC modes can be distinguished by the detection geometry and optical polarization in Raman scattering measurements [10]. In general, the frequencies of the LOPC mode are given by the solution to the equation for the frequency-dependent dielectric response of the lattice and the free electrons [4, 8, 11, 12]:

$$\varepsilon(\omega) = \varepsilon_{\infty} \left[ \frac{\Omega_{LO}^2 - \Omega_{TO}^2}{\Omega_{TO}^2 - i\Gamma\omega - \omega^2} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \right] = 0, \quad (1)$$

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LO and TO phonon frequencies. The plasma frequency, 1.5 eV light [13] observed the two E\textsubscript{2} (low-B\textsubscript{1}) and high-E\textsubscript{2} (high-B\textsubscript{1}) denote the low- and high-frequency E\textsubscript{2} (B\textsubscript{1}) modes, respectively. Numbers in parentheses denote the frequencies in THz obtained in previous studies [5, 6].

\[
\epsilon_{\infty} \text{ is the high-frequency dielectric constant, } \gamma \text{ and } \Gamma, \text{ plasmon and phonon damping rates, and } 2\Omega_{LO} \text{ and } 2\Omega_{TO}, \text{ the LO and TO phonon frequencies. The plasma frequency,}
\]

\[
\omega_p = \sqrt{\frac{n e^2}{m^* \epsilon_0 \epsilon_{\infty}}},
\]

depends on the free carrier density, \(n\), their effective mass, \(m^*\), and the vacuum dielectric constant, \(\epsilon_0\). For n-type GaN, the LOPC mode frequencies measured by Raman spectroscopy were found to follow the well-known undamped (\(\gamma = \Gamma = 0\)) solutions of equation (1) [8]:

\[
2\omega_2^2 = \omega_0^2 + 2\Omega_{LO}^2 \pm [\omega_0^2 + \Omega_{LO}^2]^2 - 4\Omega_{TO}^2 \Omega_{LO}^2]^{1/2}.
\]

For p-type GaN, by contrast, the coupling with plasmons was observed only as a slight broadening of the Raman LO peak without significant frequency shift [9]. The difference between the n- and p-type GaN was attributed to the heavy damping (\(\gamma \gg \omega_p\)) of the hole plasmon.

Detection of coherent optical phonons through transient transmission or reflectivity measurements enables monitoring of the femtosecond time evolution of carrier–phonon coupling. Depending on the excitation photon energy, the excitation pulses may or may not add photocarriers to the valence and conduction bands. A previous transient transmission study from GaN(0001) surface with nonresonant 1.5 eV light [13] observed the two E\textsubscript{2}-symmetry modes and the A\textsubscript{1}(LO) mode. Only the polar A\textsubscript{1}(LO) mode exhibited a pump power-dependent dephasing rate, confirming its strong Fröhlich interaction with the carriers photoexcited via a nonlinear three-photon process. No coherent LOPC mode, whether coupled with chemically doped or photoexcited carriers, was reported.

In the present study, we examine the electron–phonon coupling in differently doped GaN single crystals by transient reflectivity measurements with 3.1 eV light. With sub-band gap excitation we expect the coherent phonons to be excited mainly via the nonresonant Raman process; the excitation of electron–hole pairs below the band gap resonance could be made possible only by the Franz–Keldysh effect within the surface depletion region. We find that the dephasing rate of the A\textsubscript{1}(LO) phonon is increased and its frequency upshifted by doping with donor atoms, whereas the dephasing rate is increased without any frequency shift by doping of acceptor atoms. We attribute our observation to the formation of the LOPC mode coupled with chemically doped carriers. We also observe the coherent amplitude of the A\textsubscript{1}(LO) phonon to be enhanced significantly by the doping. Comparison with Raman spectra of the same samples suggests photoexcited ultrafast current in the surface depletion region is responsible for the enhancement.

2. Experimental details

The samples studied are GaN single crystal wurtzite poly-morphs grown by metal organic chemical vapor deposition (MOCVD) on (0001)-oriented sapphire substrates [14]. The nominally undoped GaN layer is 50 \(\mu\)m thick and has a defect concentration of \(\sim 1 \times 10^{16} \text{ cm}^{-3}\), which makes it slightly n-type. The Si-doped n-type GaN film of 3.4 \(\mu\)m thickness is grown with Si concentration of \(\sim 1 \times 10^{18} \text{ cm}^{-3}\) on a 1.6 \(\mu\)m thick undoped buffer layer. The p-type GaN film of 0.5 \(\mu\)m thickness is grown with Mg doping concentration of \(\sim 1 \times 10^{18} \text{ cm}^{-3}\) on a 5 \(\mu\)m thick undoped layer. Si and Mg are typical n- and p-type dopants in GaN [15, 16]. For comparison we also investigate an (0001)-oriented semi-insulating (SI) GaN single crystal of 1 mm thickness (Kyma Technologies Inc.).

Pump–probe reflectivity measurements are performed with optical pulses with \(\sim 10 \text{ fs}\) duration, 400 nm wavelength (3.1 eV energy), and 70 MHz repetition rate. Only a very small fraction (\(\sim 0.1\%\)) of the optical pulse spectrum exceeds the fundamental gap of GaN. Linearly polarized pump and probe beams are incident with angles of 20\(^\circ\) and 5\(^\circ\) from the surface normal. In this near back-reflection geometry from the (0001) surface, only the E\textsubscript{2} and A\textsubscript{1}(LO) modes are dipole-allowed by the Raman scattering selection rules, which also dominate the generation and detection of coherent phonons [17]. The pump-induced change in the reflectivity \(\Delta R\) is measured by detecting the probe beam reflected from the sample surface (isotropic detection) and accumulating the signal in a digital oscilloscope while scanning the time delay between the pump and the probe pulses at 20 Hz (fast scan).

Separate Raman scattering measurements on the same samples are performed in back-reflection geometry using a Raman microscope with nonresonant 532 nm (2.3 eV) excitation. The low-E\textsubscript{2}, high-E\textsubscript{2} and A\textsubscript{1}(LO) phonons are observed at 142, 569 and 736 cm\(^{-1}\), as shown in figure 2; these comprise all the fundamental phonon modes allowed in the back-scattering geometry from the (0001) surface. For the Si- and Mg-doped samples the A\textsubscript{1}(LO) peak splits into

\[\begin{align*}
A_1 & \quad \text{(LO 22.0, TO 16.0)} \\
\text{low-E}_2 & \quad (4.3) \\
\text{low-B}_1 & \quad (10.1) \\
E_1 & \quad \text{(LO 22.3, TO 16.8)} \\
\text{high-E}_2 & \quad (17.1) \\
\text{high-B}_1 & \quad (21.6) \\
\end{align*}\]

Figure 1. Atomic displacements of the Γ-point phonons in wurtzite GaN [6]. Gallium and nitrogen atoms are colored white and red. Low-E\textsubscript{2} (low-B\textsubscript{1}) and high-E\textsubscript{2} (high-B\textsubscript{1}) denote the low- and high-frequency E\textsubscript{2} (B\textsubscript{1}) modes, respectively. Numbers in parentheses denote the frequencies in THz obtained in previous studies [5, 6].
two, i.e., the $A_1(LO)$ phonon coupled with plasmons ($A_1$-like LOPC mode) from the doped layer and the bare $A_1(LO)$ phonon from the undoped buffer layer [4, 8–11]. For the thin film samples small Raman peaks from the dipole-forbidden $E_1(LO)$ phonon of GaN and from the sapphire substrate are also observed at 561 and 417 cm$^{-1}$.

### 3. Results and discussion

Figure 3 compares the pump-induced reflectivity change $\Delta R/R$ of differently doped GaN samples. After photoexcitation at $t = 0$, the reflectivity oscillates with a clear beating pattern. The beating is mainly contributed by the high-frequency $E_2$ mode at 17 THz and the $A_1(LO)$ mode at 22 THz, as shown in the Fourier transform (FT) spectra in figure 4. The individual oscillation components extracted by fitting the time-domain data to a sum of damped harmonic oscillations:

$$
\frac{\Delta R(t)}{R} \simeq \frac{\Delta R_A}{R} \exp(-\Gamma_A t) \sin(2\pi \Omega_A t + \psi_A) + \frac{\Delta R_E}{R} \exp(-\Gamma_E t) \sin(2\pi \Omega_E t + \psi_E),
$$

are also shown in figure 3. The observation of the $E_2$ and $A_1$-symmetry modes in the near back-reflection configuration is expected from the Raman selection rules [13, 5]. We also observe a weak low-$E_2$ mode at 4 THz and an overtone of the $A_1(LO)$ phonon ($2A_1(LO)$) at 44 THz, as shown in figure 4. The small amplitude of the $2A_1(LO)$ mode is in contrast to the resonant Raman spectrum at wavelengths shorter than 380 nm, which was found to be dominated by the overtones up to 7th [10, 18, 19]. Because our measurement system has sufficient bandwidth to detect the coherent response with bandwidth exceeding 100 THz [20], the weak overtone signal can be attributed to a pre-resonant response to photoexcitation at 400 nm. Our observation thus indicates that the resonant effect is negligible with photoexcitation at 400 nm. The origin of the $2A_1(LO)$ mode must be different from the recently reported harmonic frequency comb generation in Si through the amplitude and phase modulation of the reflected light within the optical skin depth, because the GaN samples are transparent to 3.1 eV light [20]. With increasing pump power, the amplitudes of all the coherent phonon modes increase linearly, while their dephasing rates and the frequencies
exhibit no systematic pump-power dependence for all the GaN samples examined in the present study. This confirms that multi-photon excitation of carriers is negligible under our photoexcitation with 3.1 eV light, in contrast to the near infrared photoexcitation in the previous transmission study [13].

Doping of GaN by Si and Mg impurities modifies the coherent A\textsubscript{1}(LO) mode significantly through the coupling with plasmons, whereas the high-E\textsubscript{2} mode is hardly affected, as summarized in figure 5. This is because the polar A\textsubscript{1}(LO) mode is much more susceptible to doping due to Fröhlich interaction than the non-polar E\textsubscript{2} mode [13, 18]. For the undoped sample, the dephasing rate of the A\textsubscript{1}(LO) mode is $\Gamma_A \sim 0.6$ ps\textsuperscript{−1} for the undoped sample, which is consistent with the lifetime obtained by time-resolved Raman spectroscopy at a low photocarrier density (10\textsuperscript{16} cm\textsuperscript{−3}) [3]. Doping of Si impurities (n-type) increases $\Gamma_A$ to 2.8 ps\textsuperscript{−1} and upshifts the frequency $\Omega_A$ by 0.05 THz with respect to that of the undoped sample. The Si-doping effect can be attributed to the formation of A\textsubscript{1}(LO)-electron plasma coupled mode (A\textsubscript{1}-like LOPC mode). The significant increase in $\Gamma_A$ suggests that the plasmon damping cannot be neglected. Since $\omega_p$ hardly varies with $\omega_p$ in the present low concentration regime, we calculate the theoretical Raman scattering cross section due to deformation potential and electro-optic mechanisms [21] to estimate $\omega_p$ and $\gamma$. The theoretical spectrum reproduces the experimental FT spectrum reasonably when we assume $\omega_p \sim 10$ THz and $\gamma \sim 50$ ps\textsuperscript{−1}. Doping of Mg (p-type) enhances $\Gamma_A$ likewise, but the effect is smaller than n-doping, and $\Omega_A$ is hardly affected, as shown in figures 5(a) and (b). The experimental FT spectrum is reproduced by assuming $\omega_p \sim 10$ THz and $\gamma \sim 100$ ps\textsuperscript{−1}. The obtained plasma frequencies are consistent with the carrier density $n \sim 1 \times 10^{18}$ cm\textsuperscript{−3} of the n- and p-type samples (equation (2)), and the plasmon damping rates are comparable with those obtained in the previous Raman studies on similarly doped n- and p-type GaN [4, 11]. Our observations confirm that coupling of the LO phonon with hole plasma is weaker than that with electron plasma due to the faster damping of holes [9, 11]. We note that the Faust–Henry coefficient used in the calculation was controversial among the previous studies [4, 12, 11], and the values obtained in the present study should therefore give only semiquantitative estimations.

In general, the LO phonons can couple with both chemically doped and photodoped electrons and holes. In the present study, however, we consider that the LO phonons couple mainly with chemically doped electrons and holes for Si- and Mg-doped samples, because we observe a comparable line width for the A\textsubscript{1}-like LOPC peak in our Raman scattering spectra (figure 2). We note that in the Raman spectra we clearly see the double peak due to the A\textsubscript{1}-like LOPC mode and the bare A\textsubscript{1}(LO) phonon from the doped and undoped buffer layers (figure 2), whereas in the time domain we observe only the A\textsubscript{1}-like LOPC mode from the doped layer. This is probably because the coherent polar phonons are generated much more efficiently for doped layers than for the undoped one, as we will discuss in the following paragraph.

Doping of Si or Mg also significantly enhances the amplitude of the A\textsubscript{1}(LO) mode relative to that of the high-E\textsubscript{2} mode, i.e., $\Delta R_A/\Delta R_{E2}$, whereas the Raman peak intensity ratio $I_A/I_{E2}$ is unchanged, as shown in figure 5(c). The difference can be explained in terms of the generation mechanism of the coherent A\textsubscript{1}(LO) phonon. If all the coherent phonons are solely generated via impulsive stimulated Raman scattering (ISRS) [22], the relative amplitudes should be proportional to the square root of the relative Raman intensity $\sqrt{I_A/I_{E2}}$ measured at the same wavelength. In resonant photoexcitation on polar semiconductors, however, coherent polar optical phonons can also be generated via transient depletion field screening (TDFS) mechanism [23], in which ultrafast screening by photoinjected current creates an abrupt change in the surface built-in field (figure 6(a)). In the present study, photocarriers cannot be generated in the bulk GaN, since the photon energy is slightly below the fundamental band gap. Nevertheless, in the surface depletion region of n-doped GaN, the steep band bending can induce tails of the valence and conduction bands of about 0.1 eV through the Franz–Keldysh effect [24], as schematically illustrated in figure 6(b). This would allow a small but finite fraction of the 3.1 eV light to excite the interband transition. The
photoexcited electrons would drift deeper into the bulk region, and thereby generate coherent $A_1$(LO) phonons by TDFS and form the LOPC mode. We thus attribute the enhancement in the coherent LOPC amplitude by n-doping to the additional TDFS generation. A similar mechanism can be at work at the surface of a p-type semiconductor. The difference in the generation efficiency for the n- and p-doped samples depends on the position of the Fermi level pinning with respect to the band gap edges.

4. Conclusion

We have investigated the effect of n- and p-type doping on carrier–phonon dynamics of GaN under photoexcitation with 3.1 eV light. The dephasing rate, the frequency and the amplitude of the polar $A_1$(LO) phonon are modified by coupling with chemically doped electron (hole) plasma for the n-doped (p-doped) sample, with the effect of n-doping greater than that of p-doping. Because the photon energy is slightly below the band gap of bulk GaN, photoexcitation is made possible by the Franz–Keldysh effect only at the surfaces with steep band bending. Such photoexcitation enables the generation of coherent $A_1$(LO) phonons via transient screening in the surface depletion field. Our study reveals the complex interactions between the carriers and lattice affecting the optical properties of GaN in the surface band bending region.

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