

Temperature-dependent Raman scattering in N–In codoped p-type ZnO thin films

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Abstract

We have carried out a detailed temperature-dependent Raman scattering investigation on coupled longitudinal–optical phonon–plasmon modes in N–In codoped p-type ZnO thin films with different hole densities. In combination with the theoretical analysis for the temperature-dependent frequencies, linewidths, and lifetimes, we have revealed an asymmetrical decay process with frequencies near 450 and 130 cm⁻¹, an increasing anharmonic effect with hole density, as well as a decreasing lifetime with enhanced anharmonicity. The variation in the relative contribution from three- and four-phonon processes can be further attributed to the diversification of the local phonon density of states due to N–In codoping.

ZnO is an important direct wide band gap (3.36 eV) semiconductor with large binding energy (60 meV) at room temperature and piezoelectric properties. ZnO has recently attracted considerable attention due to its promising applications for optically gated switches, blue and ultraviolet light emitting devices, photodetectors, nanomanipulators and chemical sensors [1, 2]. However, the fabrication of p-type ZnO remains a formidable challenge because of the growth difficulties such as the self-compensation effect by intrinsic defects, deep acceptor level within the band gap and low solubility of the acceptor dopants [3]. Recent research interests have mainly focused on preparing p-type ZnO, but many of its fundamental characteristics are still not well known.

It is crucial to investigate the lattice vibration properties for device structures with high current densities producing substantial Joule heating, especially for polar materials where the strong interaction between free carriers and polar longitudinal–optical (LO) phonons is dominant [4]. Raman scattering, as a fast, nondestructive and contactless technique, can directly probe the lattice vibration of semiconductors

which strongly affect the band structure and behaviour of carriers. Recently, we have explored the coupled LO phonon–plasmon modes (CPPMs) in p-ZnO and found a good agreement of hole density and mobility between room-temperature Raman spectra and Hall measurements [5]. Changes of the frequency, linewidth and lifetime of Raman mode with temperature can further provide basic information of lattice dynamics. As a result, temperature-dependent Raman spectroscopy has been widely employed in semiconductors, e.g. AlN [4], InN [6], and ternary alloys [7–10]. Nevertheless, few studies are reported for detailed investigation on the temperature dependence of Raman scattering of ZnO [10, 11]. To the best of our knowledge, little information is available so far regarding temperature dependence of the CPPM behaviour in p-type ZnO.

In this paper, we have presented a comprehensive investigation of temperature-dependent Raman spectra of the CPPM in N–In codoped p-type ZnO films with different hole densities grown by ultrasonic spray pyrolysis (USP) in the temperature range from 83 to 578 K. Through detailed theoretical modelling for the frequency downshift and

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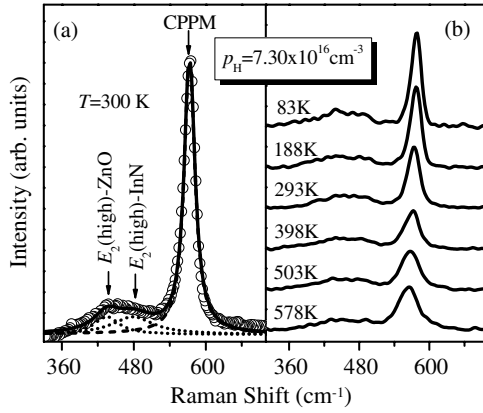


Figure 1. (a) Room-temperature experimental (○) and calculated (—: total fits; ·····: Lorentzian fit; - - -: the CPPM model calculation) Raman spectrum, and (b) temperature-dependent Raman spectra from a p-type ZnO with hole density of $7.30 \times 10^{16} \text{ cm}^{-3}$.

linewidth broadening, we have determined the decay process of the CPPM, where the anharmonic effect on the frequency, linewidth and lifetime has been clearly illustrated.

N–In codoped p-ZnO thin films were grown by the USP method in air atmosphere [3]. Three kinds of aqueous solution, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (AR, 0.5 mol l^{-1}), $\text{CH}_3\text{COONH}_4$ (AR, 2.5 mol l^{-1}), and $\text{In}(\text{NO}_3)_3$ (AR, 0.5 mol l^{-1}), were chosen as the sources of zinc, nitrogen and indium, respectively. Intrinsic crystalline Si (*c*-Si) (100) wafers with a conductivity of $2.94 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ were used as the substrates, which were etched by diluted HF (10%) for 3 min prior to the deposition. The aerosol of the precursor solution was generated by the commercial ultrasonic nebulizer and transported to the substrate heated at 450°C . The atomic ratio of Zn/N/In was 1 : 3 : 0.05 in the precursor solution, and the different doping concentrations in the N–In codoped films were realized by the change of the deposition rate which was controlled by the carrier gas flow rate and the power of the ultrasonic nebulizer. Temperature-dependent micro-Raman scattering spectra were performed with the 325 nm line of a He–Cd laser, and recorded in a backscattering geometry of $z(x, -)z$ configuration using a Jobin Yvon LabRAM HR 800UV micro-Raman system with an Andor DU420 classic CCD detector and a Linkam THMS600 temperature stage. Hole density of the same samples subjected to the Raman probes were characterized by the magnetic field dependent (0–0.6 T) Hall measurements at room temperature, which were performed in the Van der Pauw configuration by a set of Keithley Hall instruments.

Figure 1(a) presents the room-temperature Raman spectrum of a p-type ZnO sample with hole density of $7.30 \times 10^{16} \text{ cm}^{-3}$. We have assigned the modes at $\sim 434 \text{ cm}^{-1}$ (dotted curve), $\sim 488 \text{ cm}^{-1}$ (dotted curve) and $\sim 570 \text{ cm}^{-1}$ (dashed curve) to the $E_2(\text{high})$ mode of ZnO, $E_2(\text{high})$ mode of InN, and CPPM of p-type ZnO, respectively [5]. In the following, we focus on the temperature dependences of the frequency, linewidth and lifetime of the CPPM in N–In codoped p-type ZnO. We select six samples with different hole densities of 7.30×10^{16} , 1.29×10^{17} , 2.46×10^{17} , 3.64×10^{17} , 1.10×10^{18} and $2.30 \times 10^{18} \text{ cm}^{-3}$. Figure 1(b) shows the Raman spectra of the CPPM in the p-type ZnO sample with a hole density of $7.30 \times 10^{16} \text{ cm}^{-3}$ from 83 to 578 K. It can be seen that the

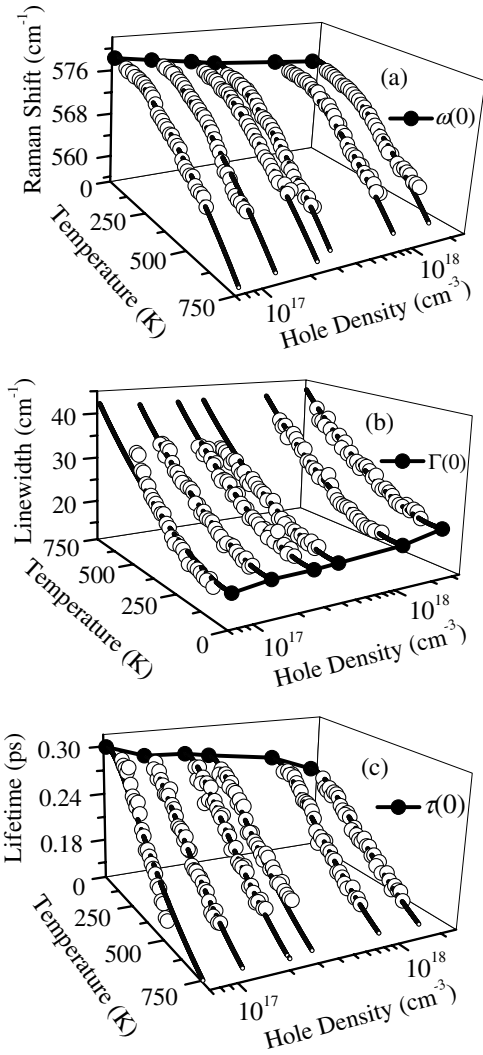


Figure 2. Temperature-dependent (a) Raman frequency $\omega(T)$, (b) linewidth $\Gamma(T)$ and (c) lifetime $\tau(T)$ for the CPPM in p-type ZnO with different hole densities (○). Solid curves are the theoretical fits to equations (1)–(4). The filled circles represent (a) Raman frequencies at 0 K [$\omega(0)$], (b) linewidths at 0 K [$\Gamma(0)$] and (c) lifetimes at 0 K [$\tau(0)$].

CPPM shifts to lower frequency and broadens with the increase of temperature. In order to accurately determine the Raman frequency and linewidth of the CPPM, we have employed Lorentzian lineshape to fit the CPPM peaks (calculated from the CPPM model [5]) throughout the measured temperature range. The temperature-dependent frequencies and linewidths of the CPPM in p-type ZnO with different hole densities are presented as open circles in figures 2(a) and (b).

The downshift of the Raman frequency with the increase in temperature is mainly due to the effects of thermal expansion, lattice-mismatch-induced strain and anharmonic coupling to other phonons. The temperature-dependent Raman frequency $\omega(T)$ can be expressed as [6, 8]

$$\omega(T) = \omega_0 + \Delta\omega_e(T) + \Delta\omega_s(T) + \Delta\omega_d(T), \quad (1)$$

where ω_0 is the harmonic frequency, $\Delta\omega_e(T)$ is the contribution of thermal expansion or volume change, $\Delta\omega_s(T)$ comes from the lattice and thermal mismatch between the

Table 1. The best fitting parameters (with errors less than 0.5%) for Raman frequency (equations (1) and (2)), linewidth (equation (3)), and lifetime (equation (4)) of the CPPM in p-type ZnO.

p_H (cm^{-3})	ω_0 (cm^{-1})	M_1 (cm^{-1})	M_2 (cm^{-1})	Γ_0 (cm^{-1})	N_1 (cm^{-1})	N_2 (cm^{-1})	$\tau_{\text{anharmonic}}$ (ps)		
							83 K	308 K	578 K
7.30×10^{16}	580.03	-1.47	-0.36	14.97	2.05	0.70	1.70	0.65	0.29
1.29×10^{17}	579.13	-1.49	-0.38	15.64	2.11	0.74	1.66	0.64	0.28
2.46×10^{17}	578.16	-1.50	-0.39	15.93	2.15	0.77	1.64	0.63	0.28
3.64×10^{17}	577.50	-1.52	-0.42	16.26	2.16	0.79	1.58	0.60	0.26
1.10×10^{18}	576.70	-1.57	-0.52	16.97	2.24	0.88	1.53	0.58	0.25
2.30×10^{18}	576.17	-1.61	-0.56	18.73	2.26	0.91	1.51	0.57	0.24

ZnO thin film and Si substrate and $\Delta\omega_d(T)$ is the one due to the anharmonic coupling to phonons of other branches. The term $\Delta\omega_c(T)$ can be given by $\Delta\omega_c(T) = -\omega_0\gamma \int_0^T [\alpha_c(T') + 2\alpha_a(T')]dT'$, with γ the Grüneisen parameter, α_c and α_a the parallel and perpendicular temperature-dependent coefficients of linear thermal expansion, respectively [12]. Here, we employ the Grüneisen parameter of the $A_1(\text{LO})$ mode [13], due to a phonon-like character of the CPPM in p-type ZnO [14]. The strain-induced term $\Delta\omega_s(T)$ can be written as $\Delta\omega_s(T) = [2a - (2C_{13}/C_{33})b]\varepsilon(T)$, where $\varepsilon(T)$ is a temperature dependence of in-plane strain for the different thermal expansion coefficients between the thin film and the substrate [15]. The phonon deformation potentials a and b are assumed to be the same as those of $E_2(\text{high})$ [16] because those of $A_1(\text{LO})$ are not available. The elastic constants C_{13} and C_{33} of ZnO are taken from [17].

For the anharmonic coupling term $\Delta\omega_d(T)$, we can describe it by taking into account cubic and quartic terms in the anharmonic Hamiltonian as [4, 6–10]

$$\Delta\omega_d(T) = M_1[1 + n(T, \omega_1) + n(T, \omega_2)] + M_2[1 + 3n(T, \omega_0/3) + 3n^2(T, \omega_0/3)], \quad (2)$$

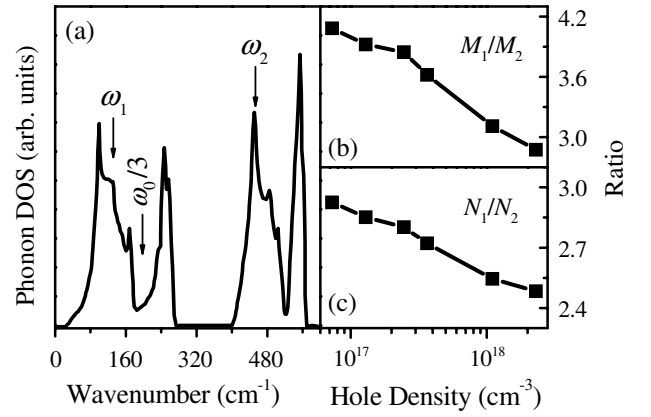
where $n(T, \omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ is the Bose-Einstein function. The first term is the decay into two phonons of frequency ω_1 and ω_2 (three-phonon process), with $\omega_1 + \omega_2 = \omega_0$; while the second term represents the decay into three phonons (four-phonon process), assumed to be of equal frequency $\omega_0/3$ for simplicity. M_1 and M_2 are anharmonic constants which identify the relative probability of the occurrence of each process.

The phonon broadening $\Gamma(T)$ arises mainly from inhomogeneous impurity phonon scattering and anharmonic decay. Similar to the temperature dependence of Raman shift, the phonon broadening can be described by assuming the decay into two phonons with frequency ω_1 and ω_2 and the symmetric decay into three phonons again [4, 6–10]:

$$\Gamma(T) = \Gamma_0 + N_1[1 + n(T, \omega_1) + n(T, \omega_2)] + N_2[1 + 3n(T, \omega_0/3) + 3n^2(T, \omega_0/3)], \quad (3)$$

where Γ_0 is attributed to inherent defect or impurity scattering. The second term is induced by the asymmetric decay of the three-phonon process, while the third term represents the symmetric decay of four-phonon process. Anharmonic constants N_1 and N_2 also confirm the relative probability of the occurrence of each process.

Equations (1) and (2) have been used to fit the temperature dependence of Raman frequencies $\omega(T)$ for the CPPM in these


Figure 3. (a) Calculated phonon DoS in ZnO, with the positions of ω_1 , ω_2 and $\omega_0/3$ marked. (b) M_1/M_2 and (c) N_1/N_2 (■) as a function of hole density in p-type ZnO.

p-type ZnO samples with the fitting parameters ω_0 , ω_1 , ω_2 , M_1 and M_2 . Figure 2(a) shows good agreement between the theoretical fit (solid curves) and the experimental data (open circles), where Raman frequencies at 0 K [$\omega(0)$] of the CPPM (filled circles) are also displayed. Figure 2(b) exhibits the temperature dependence of linewidths $\Gamma(T)$ for the CPPM in the p-type ZnO samples (open circles) with the least-squares fit of equation (3) (solid curves) by varying parameters ω_1 , ω_2 , Γ_0 , N_1 and N_2 . Filled circles in figure 2(b) represent the linewidths at 0 K [$\Gamma(0)$] of the CPPM. The fitting parameters of ω_0 , M_1 , M_2 , Γ_0 , N_1 and N_2 are summarized in table 1. It is noted that the values of $\omega_1 \sim 450 \text{ cm}^{-1}$ and $\omega_2 \sim 130 \text{ cm}^{-1}$ obtained from Raman frequencies are coincident with those from linewidths, which manifests the asymmetric decay process for the CPPM. In order to exactly understand the decay mechanism, we resort to the phonon dispersion curves [13]. A symmetric decay of the CPPM is completely not possible because of the rather large energy gap between the acoustic and the optical phonon branches for ZnO. But an asymmetric decay of the CPPM into one transverse optical (TO) and one longitudinal acoustic (LA) phonon on the $\Gamma-K$ or $\Gamma-M$ line of the Brillouin zone is allowed, which supports our experimental results. In addition, from the phonon density of states (DOS) [13] shown in figure 3(a), we can find a sizable magnitude of the phonon DOS at ω_1 and ω_2 , further demonstrating that this asymmetric decay into phonons with frequencies near 450 and 130 cm^{-1} is reasonable.

The anharmonic constants M_1 , M_2 , N_1 and N_2 increase with hole density, which manifests the enhancement of anharmonic effect. From figures 2(a) and (b), we can also

see that temperature-dependent changes in frequencies and linewidths increase with hole density. In N–In codoped p-type ZnO, the increasing impurity-induced disorder with the hole density brings an increase of phonon DOS, resulting in an increase in the probability of inelastic (anharmonic) scattering between phonons and the substitutional atoms. As a result, the contribution from anharmonicity due to impurity-induced disorder prevails with increasing hole density. On the other hand, larger numbers of phonons are produced with increasing temperature, which also lead to an increased probability of inelastic (anharmonic) scattering between phonons and the substitutive atoms. As the number of the substitutive atoms increases, the probability of inelastic decay of phonons will become larger. Thus the impurity-induced disorder anharmonicity becomes more obvious with the increase in temperature in these N–In codoped p-type ZnO.

Figures 3(b) and (c) show the ratios of M_1/M_2 and N_1/N_2 which are the relative contributions of the three-phonon and four-phonon processes to the total phonon decay. The consistency between variations of M_1/M_2 and N_1/N_2 again indicates the reliability of our results obtained from the theoretical fit of the CPPM. From the ratios of M_1/M_2 and N_1/N_2 , it is clear that the decay into two phonons is the dominant process while the four-phonon process makes minor contribution in the anharmonic coupling of the CPPM in p-type ZnO at low hole density. This phenomenon is consistent with the calculated phonon DOS shown in figure 3(a), where the weak phonon DOS at $\sim 193 \text{ cm}^{-1}$ shows less probability of the four-phonon process. With increasing hole density, the reduced ratios of M_1/M_2 and N_1/N_2 imply that the probability of four-phonon process increases while the one of three-phonon process reduces. This change of ratios can be ascribed to the variation of phonon DOS. The codoping of N and In in p-type ZnO causes lattice defect and structural disorder, which break down the translational symmetry of ZnO. In addition to the Brillouin zone-centre phonons, the phonons at Brillouin zone-edges can also contribute to the first-order Raman scattering. Reference [18] has shown the increase of the local phonon DOS in N⁺-implanted ZnO at $\sim 200 \text{ cm}^{-1}$. Therefore, we can conclude that the increasing probability of four-phonon process is due to the increasing quantity of N–In codopant, though the three-phonon process is adequately responsible for the anharmonic shift and broadening of the CPPM in the p-type ZnO samples.

Finally, it is well known that the linewidth broadening in Raman scattering is usually related to the lifetime $\tau(T)$ of the decay processes, which can be determined by [9]

$$\Gamma(T) = 1/2\pi c\tau = 1/2\pi c\tau_{\text{elastic}} + 1/2\pi c\tau_{\text{anharmonic}}, \quad (4)$$

where c is the velocity of light, $1/2\pi c\tau_{\text{elastic}} (= \Gamma_0)$ comes from elastic scattering and $1/2\pi c\tau_{\text{anharmonic}} (= N_1[1 + n(T, \omega_1) + n(T, \omega_2)] + N_2[1 + 3n(T, \omega_0/3) + 3n^2(T, \omega_0/3)])$ comes from anharmonic decay. Figure 2(c) displays the lifetimes $\tau(T)$ of the CPPM in these p-type ZnO samples (open circles) as a function of temperature, and the solid curves are the best theoretical fits. The lifetimes at 0 K [$\tau(0)$] are shown as filled circles in figure 2(c). The values of anharmonic decay time $\tau_{\text{anharmonic}}$ of the CPPM are given in table 1. We find a significant shortening of CPPM lifetime with the increase

in lattice temperature and impurity-induced disorder. This is reasonable since the anharmonicity due to disorder and temperature accelerates the decay of the CPPM in p-type ZnO.

In summary, detailed Raman spectra of N–In codoped p-type ZnO with different hole densities have been investigated in the temperature range from 83 to 578 K, with the emphasis on the CPPM. The temperature-dependent frequencies and linewidths of the CPPM in p-type ZnO can be well described by a model including the contributions of the thermal expansion, the strain between ZnO thin film and Si substrate, as well as three- and four-phonon decay. The fitting results exhibit an asymmetrical decay into a TO and a LA phonon for the CPPM and the anharmonic effect due to temperature and impurity-induced disorder. The anharmonic constants increase with hole density and the lifetime reduces with increasing anharmonicity. Furthermore, it is found that the contribution of four-phonon process increases while that of three-phonon process reduces with increasing hole density, which can be attributed to the increase of local phonon DOS due to N–In codoping.

Acknowledgments

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