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Confined phonons and phonon-mode properties of III–V nitrides with wurtzite crystal structure

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Abstract

Stimulated by the recent interest in the use of nitride-based III–V wurtzite structures for optoelectronic and electronic devices, this paper reports on the application of the Loudon model for uniaxial crystals to derive the Fröhlich interaction Hamiltonian as well as the electron–optical-phonon scattering rate in wurtzite crystals. This paper also presents experimental analyses of the mode behavior of phonons in wurtzite crystals. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Phonons in wurtzite structures; Loudon model; Nitride-based III–V structures

This paper discusses recent applications of the Loudon model [1,14] of uniaxial crystals to derive the Fröhlich interaction Hamiltonian as well as the electron–optical-phonon scattering in wurtzite crystals [2]. These results demonstrate that the optical phonon branches support mixed longitudinal and transverse modes due to the anisotropy of the wurtzites. The scattering rates due to longitudinal-like modes are similar to those obtained with the cubic Fröhlich Hamiltonian; however, those due to the transverse-like modes can be strongly enhanced relative to the cubic case over a range of angles with respect to the *c*-axis. These results have recently been extended to the case of dimensionally confined wurtzite systems and it is found that there is a complex spectrum of confined phonon modes for the III–V nitrides of wurtzite crystal structure [3]. Preliminary theoretical [4] and experimental [5] analyses of the mode behavior of phonons in wurtzite crystals is also presented. This model demonstrates that the optical phonon branches support mixed longitudinal and transverse modes due to the anisotropy of the wurtzites. Numerical results show that the scattering rates due to longitudinal-like modes are similar to those obtained with the cubic Fröhlich Hamiltonian, but those due to the transverse-like modes can be strongly enhanced relative to the cubic case over a range of angles with

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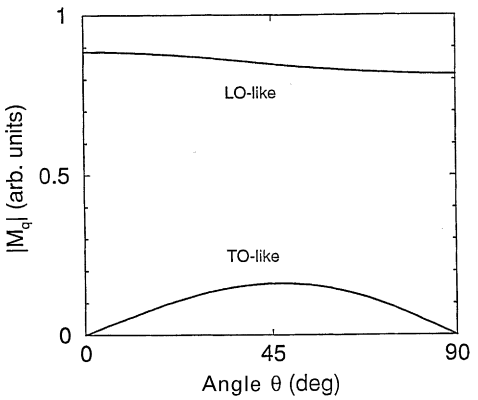

Fig. 1. Absolute value of the optical-phonon absorption in bulk wurtzite GaN as a function of the angle between the c-axis of the wurtzite structure and the phonon wave vector, $\boldsymbol{q}$.

respect to the c-axis. These trends are evident in Fig. 1 where the absolute value of the matrix element, M_q, for optical-phonon absorption in bulk wurtzite GaN is plotted as a function of the angle between the optical-phonon wave vector $\boldsymbol{q}$ and the c-axis of the crystal. The dominance of the LO-like modes in these scattering processes has been supported experimentally by subpicosecond time-resolved Raman spectroscopy [6,7]. In the dimensionally confined wurtzite systems [3], there is a complex spectrum of confined phonon modes for the III–V nitrides (III-N) of wurtzite crystal structure, more complicated than the corresponding modes in crystals of cubic symmetry. When the product of the parallel and perpendicular dielectric constants in a heterolayer are negative, oscillating phonon modes occur; however, when this product is positive, the phonon modes are damped. The parallel direction is taken to be along the z-axis which coincides with the c-axis of the wurtzite material. Fig. 2 presents such results for AlN-, GaN-, and InN-based heterostructures; the cross-hatched regions denote oscillating modes and the regions with horizontal arrows are those with decaying modes such as the interface (IF) phonon modes. There is yet to be a body of experimental work directed at understanding the confined phonons in dimensionally confined wurtzite structures.

Analyses of the mode behavior of phonons in wurtzite crystals reveal that the single-mode behavior is frequently manifested in ternary nitride-based structures. This one-mode behavior can be understood qualitatively in view of the fact that the nitrogen mass is significantly less than the mass of the other ions; accordingly, the nitrogen ions oscillate with one frequency with respect to planes of mixed

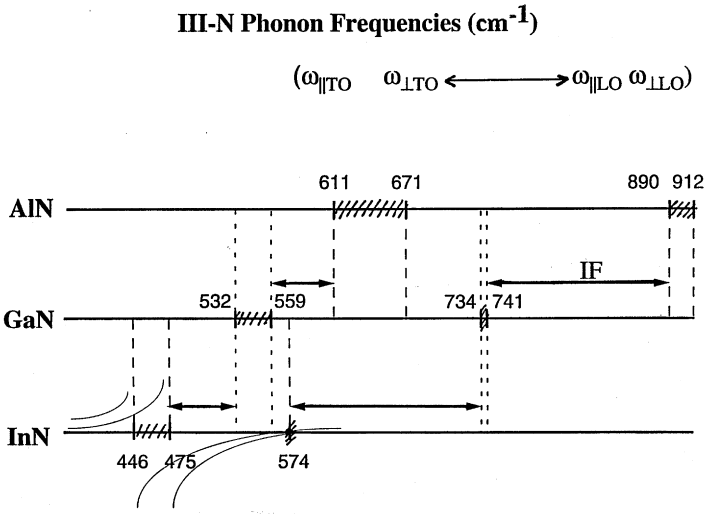

Fig. 2. Frequency intervals where oscillating and damped phonon modes occur in AlN-, GaN-, and InN-based wurtzite heterostructures. The cross-hatched regions support oscillating modes and the regions denoted by horizontal arrows support decaying modes.

group III elements. Recent first-order Raman scattering measurements in GaN made from isotopically pure ^{15}N and natural N (99.63% ^{14}N), show [8] that the Raman frequencies of the A_1(TO, LO) and E_1(TO, LO) modes shift as expected according to the inverse square root of the reduced masses; however, the E_2 modes do not follow this scaling and it appears that these modes involve mixed Ga and N vibrations. Demangeot et al. [9] analyzing Raman data on $Ga_{1-x}Al_xN$ based on a generalized dielectric model for coupled LO modes have obtained support for the apparent one-mode behavior of the polar LO phonons.

Raman spectroscopy of $Al_xGa_{1-x}N$ films, grown on SiC substrates at 1100°C via chemical vapor deposition, has been utilized in order to study the order and stress state [10,11]. Fig. 3 shows the room-temperature Raman spectra of the E_2 line from AlGaN films of various compositions. The spectral line shape exhibits asymmetric broadening and a peak shift toward higher frequency. Possible line broadening mechanisms applicable to alloys include thermal broadening, activation of a symmetry forbidden zone-center ($\boldsymbol{q} \cong 0$) mode which lies in the same frequency range as the investigated line, and broadening due to activation of a collection of modes of wavevectors $\boldsymbol{q} \cong 0$. A more plausible mechanism to account for the high-frequency asymmetric line width in the Raman spectra is the spatial correlation model [12,13]. The foundation of the model lies in attributing the relaxation of the $\boldsymbol{q} \cong 0$ Raman selection rules to the phonon confinement in a finite domain of size L, which is the average size of the ordered domains embedded in the configurational-disordered matrix.

The AlGaN films have uniformly distributed low crack density. The Raman peak position depends on the combined effects of the stress, the relaxation of the $\boldsymbol{q} \cong 0$ selection rules and the mode-type. Micro-Raman spectra were acquired at the crack regions, where the film is relatively relaxed, and at regions remote from the cracks, where the film is strained. The average peak position of the strained regions exhibits a shift of $\sim 3\ cm^{-1}$ towards lower frequencies relative to the peak of the relaxed regions suggesting that the original stress state of the film is tensile. The tensile stress in the alloys is attributed to the difference in the thermal

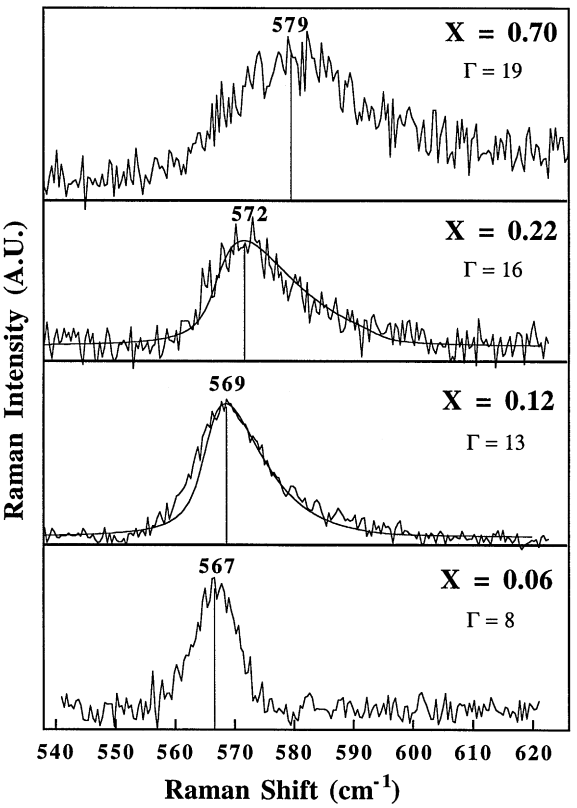

Fig. 3. The RT Raman spectra of the E_2 mode of $Al_xGa_{1-x}N$ films of composition $x = 0.06, 0.12, 0.22$ and 0.70. The respective line widths are: 8, 13, 16, and 19 cm^{-1}, and peak positions at: 567, 569, 572, 579 cm^{-1}. The solid lines superimposed on the spectra of films: $x = 0.12$ and 0.22 were calculated from the spatial correlation model.

expansion coefficients between the 6H–SiC substrate and film [11]. Fig. 4 depicts the Raman peak position as a function of the composition: after taking into account the $\sim 3\ cm^{-1}$ due to stress it is evident from the figure that the E_2 mode exhibits a two-mode behavior.

The asymmetric behavior of the E_2 Raman line shape of AlGaN alloys can be attributed to the activation of phonons of $\boldsymbol{q} \cong 0$ arising from the disordered state of the alloys. X-ray diffraction supports the Raman findings: the superlattice relative line intensity is weak. The alloy films exhibit tensile stress which is suggested to be due to interfacial thermal mismatch. The E_2 mode was found to follow a two-mode behavior of possibly small deviation ~ 3–$5\ cm^{-1}$ due to the tensile stress.

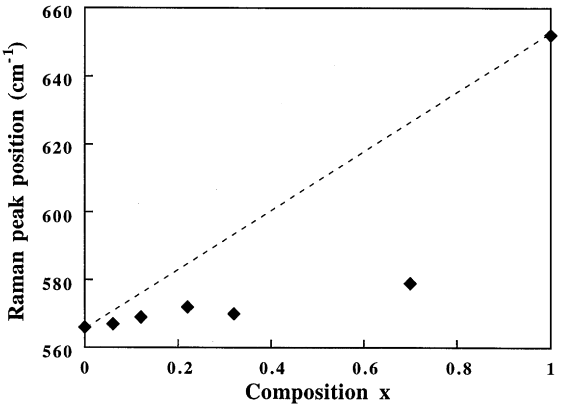

Fig. 4. The E_2 Raman peak position as a function of alloy composition x. The dashed line presents an hypothetical one-mode behavior.

These results provide a partial foundational basis for the many recent works in electronics and opto-electronics based on wurtzite structures.

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