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Ab initio study of phonons in wurtzite $Al_xGa_{1-x}N$ alloys

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We present a theoretical study of the zone-center optical phonons in wurtzite $Al_xGa_{1-x}N$ alloys over the whole compositional range from pure GaN to pure AlN. The phonon modes are broadened upon alloying and their frequencies display a blue shift with increasing Al concentration. The E_2 and E_1(TO) modes display a two-mode like behavior and do not preserve a well-defined symmetry in the alloy but rather are mixed and have a large broadening. The LO modes, instead, display a one-mode behavior and have a well-defined symmetry, small broadening, and a pronounced dependence of the frequency upon alloy composition. Therefore, we propose them as the best candidates for the compositional characterization of these materials. © *2000 American Institute of Physics.* [S0003-6951(00)04815-4]

Because of their potential for application in optoelectronic devices operating in the spectral region from the visible to the ultraviolet, the group III nitrides are currently the subject of intensive investigation. In particular, $In_xGa_{1-x}N$ and $Al_xGa_{1-x}N$ alloys are used in the active region of most nitride-based devices.[1,2] The growth of these alloys has been difficult, mainly due to the lack of lattice-matched substrates, and therefore their fundamental properties have been difficult to establish. With recent developments in growth techniques and the consequent improvement in film quality a better characterization is to be anticipated, but still remains at an early stage. For instance, detailed knowledge of the vibrational properties of nitrides ternary alloys, at present only partial,[3–6] will prove valuable for characterization of material quality as has been the case for other semiconductor solid solutions.[7–9]

For the hexagonal $Al_xGa_{1-x}N$ alloy system, a Raman study[3] for Al content x less than 0.15 concluded that this alloy system displays a ''one-mode behavior.'' More recently, the whole range of x has been covered.[4,5] The A_1 and E_1 LO modes, as well as the B_1 mode, which manifests itself by an interference with an unidentified continuum,[5] show a one-mode behavior. The E_2 modes instead display a ''two-mode behavior,'' while the behavior of the A_1(TO) mode could not be clearly established. Recent IR reflectance measurements demonstrated two-mode behavior for the E_1(TO) mode.[6]

In this letter, we give a detailed description of the zone center phonons of the wurtzite $Al_xGa_{1-x}N$ alloys over the whole range of Al concentration x, providing information useful for the compositional characterization of this system. Our calculations are based on *ab initio* interatomic force constants (IFC); the dynamical properties of the alloy are treated within the mass approximation and disorder in the alloy is simulated using large supercells.

State-of-the-art density-functional perturbation theory[10] provides an accurate and efficient way to compute the vibrational properties of crystalline materials. For an alloy, this technique can become impractical because large supercells are needed to simulate the effects of disorder. However, due to the chemical similarity between the cation species, there are only small differences in the IFC of GaN and AlN. It is therefore possible to give an accurate description of the vibrational properties of the pure materials and their alloys using a single set of interatomic force constants and taking into account only the difference in atomic mass of the different cations (mass approximation). This approximation has been very successful in the description of the vibrational properties of $Al_xGa_{1-x}As$ solid solutions[8] and superlattices.[9]

For the present study, the alloy IFCs are obtained as simple averages of the interatomic *ab initio* force constants computed for GaN and AlN in Ref. 11. We verified that the mass approximation provides an accurate description of the vibrational properties for the two pure materials. In Fig. 1, the phonon dispersions of GaN and AlN computed using the present approach are compared to the full self-consistent calculations from Ref. 11. The LO modes are the most sensitive to the mass approximation; they are shifted upwards in GaN and downwards in AlN. The optical frequencies of the alloy are described to within an accuracy of better than 4%.

To describe the phonons of the alloy system, we computed the dynamical matrices of large supercells containing

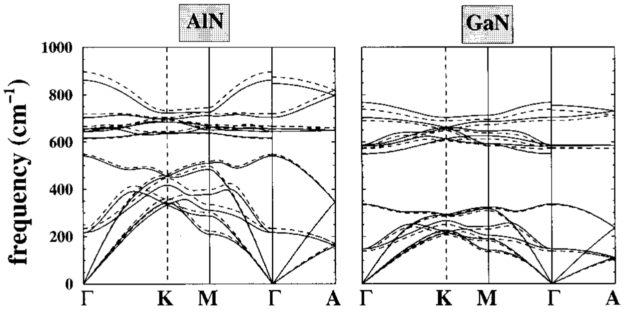

FIG. 1. Phonon dispersions for wurtzite AlN and GaN, computed with the mass approximation (solid lines), are compared with the full self-consistent *ab initio* phonon dispersions from Ref. 11 (dashed lines). The optical modes are the most sensitive to the mass approximation; the discrepancy is less than 4%.

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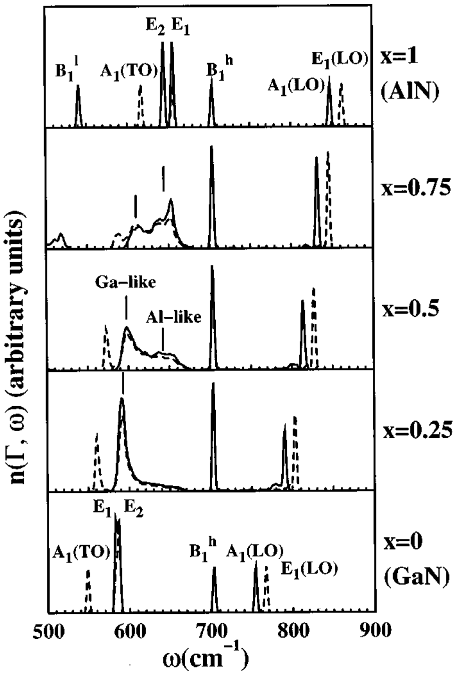

FIG. 2. Spectral density of states (SDOS) of the zone-center optical phonons in AlGaN alloys for several aluminum concentrations x. Solid lines indicate modes with wave vector parallel to the c axis ($\Gamma_{\parallel}$) and dashed lines indicate modes with wave vector perpendicular to the c axis ($\Gamma_{\perp}$).

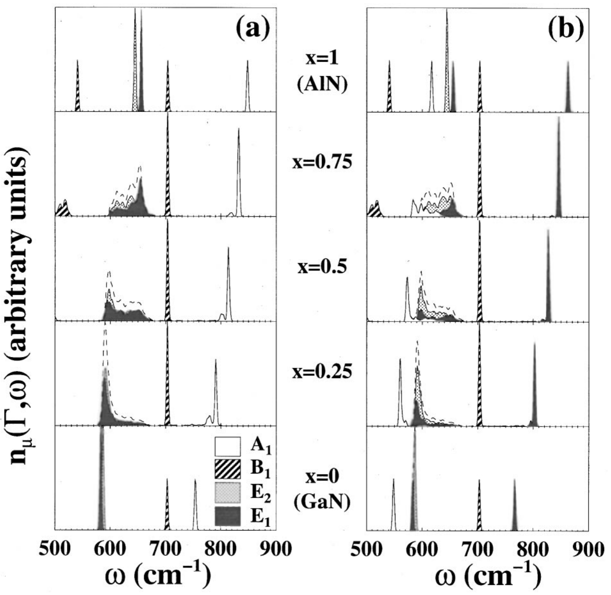

FIG. 3. Total SDOS (dashed line) decomposed into the partial SDOS corresponding to the four symmetries A_1, B_1, E_2, and E_1 for several aluminum concentrations x: (a) modes at $\Gamma_{\parallel}$, (b) modes at $\Gamma_{\perp}$.

1024 atoms in which the cation sites are occupied at random by Al ions with probability x and Ga ions with probability $(1-x)$. We then diagonalized these dynamical matrices at the zone center of the supercell BZ. Due to the BZ folding, the zone center of the supercell corresponds to several $\mathbf{q}$ vectors of the elementary bulk cell. To extract information at a particular $\mathbf{q}$ vector in the wurtzite BZ, we computed the spectral density of states (SDOS)

$$n(\mathbf{q},\omega)=\sum_{\mu} n_{\mu}(\mathbf{q},\omega), \tag{1}$$

where the partial spectral density of states (PSDOS),

$$n_{\mu}(\mathbf{q},\omega)=\sum_{\nu,i} \delta(\omega-\omega_{\nu})|\langle \mathbf{q},\mu,i|\xi_{\nu}\rangle|^2, \tag{2}$$

is the contribution of modes of a given symmetry, μ, to the SDOS. The ξ's are the vibrational eigenvectors of the alloy supercell, ω_ν are the corresponding frequencies, and $|\mathbf{q},\mu,i\rangle$ is a normalized vector of wave vector $\mathbf{q}$ with the symmetry of the irreducible representation μ of the wurtzite group. The sum on i runs over all the vectors belonging to the irreducible representation μ. For a given $\mathbf{q}$ vector, the SDOS gives the density of phonons of frequency ω. For practical purposes, the δ function is approximated by a Gaussian of width equal to 2 cm^{-1}.

We focus our attention on the optical phonons at the zone center: in Fig. 2, we show the SDOS computed at Γ over the range of frequencies of the optical modes, for five values of the Al concentration $0 \leqslant x \leqslant 1$. To analyze the symmetry of the modes, we computed the PSDOS that is shown in Fig. 3.

At the Γ point of the pure materials, there are four optical modes: A_1, B_1, $E_1^{(2)}$, and $E_2^{(2)}$. The A_1 and $E_1^{(2)}$ modes are both Raman and infrared active, the $E_2^{(2)}$ mode is only Raman active, while the B_1 mode is silent. Due to the macroscopic electric field associated with the atomic displacements of the longitudinal optical phonons, the A_1 and $E_1^{(2)}$ optical modes are split into LO and TO components. Furthermore, as a result of the anisotropic nature of the wurtzite structure, these modes have an angular dependence. In particular, approaching Γ from the ΓA direction parallel to the c axis ($\Gamma_{\parallel}$), the A_1 mode is LO, while the two degenerate E_1 modes are TO; on the other hand, approaching Γ from a direction perpendicular to the c axis ($\Gamma_{\perp}$), the A_1 mode is transverse, while one of the E_1 modes is longitudinal and the other is transverse.

As in the pure materials, we find that the $Al_xGa_{1-x}N$ alloy has one A_1(LO) mode and one E_1(LO). The corresponding peaks in the SDOS are narrow, indicating that the LO modes in the alloy have a well-defined frequency. Furthermore, with increasing aluminum concentration, each LO frequency is shifted towards a larger value by about 100 cm^{-1} from its value in GaN to its value in AlN. Consequently, the A_1(LO) and E_1(LO) modes are good candidates for the characterization of the alloy composition. The ''silent'' B_1 mode displays a similar behavior; the alloy has only one B_1 mode with a well-defined frequency. However, since the B_1 frequency in GaN is very close to the one in AlN, it is almost independent of alloy composition.

The E_2 and E_1(TO) modes behave differently. A broad feature in the SDOS corresponds to these modes, indicating that there are no E modes of well-defined frequency in the alloy. The PSDOS (see Fig. 3) shows that the E modes do not have defined symmetry either, having contributions of E_2, E_1, and, to some extent in the Al-rich region, A_1 symmetry. In an alloy, disorder breaks the symmetry of the modes. Furthermore, the $\mathbf{q}$ vector is no more strictly conserved, although it is still possible to have a dispersion. Because the E modes of GaN and, in particular, of AlN are so flat and close in energy, modes of different symmetry and $\mathbf{q}$ vector can mix; this magnifies the effect of the disorder on

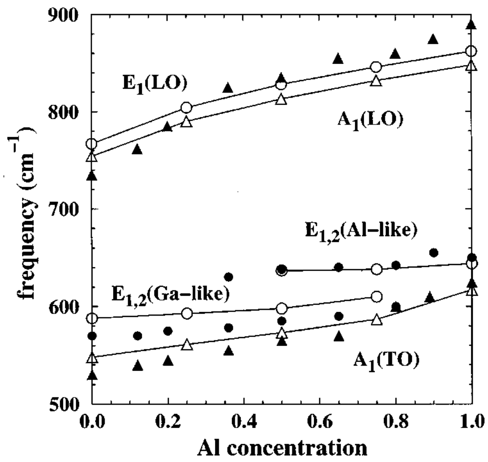

FIG. 4. Frequencies of the zone-center optical phonons in $Al_xGa_{1-x}N$ alloys as a function of the Al concentration x. Empty symbols represent our theoretical results; filled symbols represents experimental data from Ref. 4. Triangles: A_1 modes; circles: E modes.

the modes and produces the broad band. In spite of this, one can still identify two main structures that correspond to the E modes of GaN and AlN, respectively. With increasing Al concentration, the intensity of the GaN E mode decreases and the intensity of the AlN E mode increases; this is reminiscent of a two-mode behavior.

In Fig. 2, there is one clear peak corresponding to the A_1(TO) mode, that is situated just below the E modes. With increasing Al concentration, its frequency increases and its intensity decreases. The former is typical of a one-mode behavior; however, the latter is rather typical of a two-mode behavior. Further insight can be gleaned from Fig. 3(b). We have an A_1(TO) mode with a well-defined frequency that blueshifts with increasing Al concentration from its value in pure GaN. Along with this shift, we see a corresponding decrease in the intensity of the mode and the appearance and growth of a very broad A_1(TO) feature in the AlN frequency region. This suggests a two-mode behavior also for this mode, with strong symmetry mixing with E_1 and E_2 modes in the Al-rich region.

In Fig. 4, we report the position of the peaks in the SDOS as a function of the Al concentration and compare them with the available Raman data.[4,5] For the E modes that do not have a well-defined frequency in the alloy, we report the position of the main peaks of the broad band as indicated in Fig. 2. For the A_1(TO), we report only the value of the sharper peak, because the broader feature is mixed with the E modes. The agreement of our results with the Raman data[4,5] is very good. The systematic overestimation (underestimation) of the frequencies for Ga-rich (Al-rich) alloys is due to the mass approximation.

To summarize, we have characterized the behavior of the zone-center optical phonons in the $Al_xGa_{1-x}N$ alloys over the whole compositional range from pure AlN to pure GaN. The phonon modes are broadened upon alloying and their frequencies display a blueshift with increasing Al concentration. The A_1(LO) and E_1(LO) modes have a one-mode behavior and are the best candidates for the compositional characterization of this system as they have a well-defined symmetry, small broadening and a pronounced dependence upon alloy composition. The E_2 and E_1(TO), and to some extent, the A_1(TO) modes have a two-mode behavior and do not preserve a defined symmetry upon alloying but are mixed and display a large broadening that increases with increasing Al concentration. Our results explain well the available experimental data and provide important information for the compositional characterization of this alloy.

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