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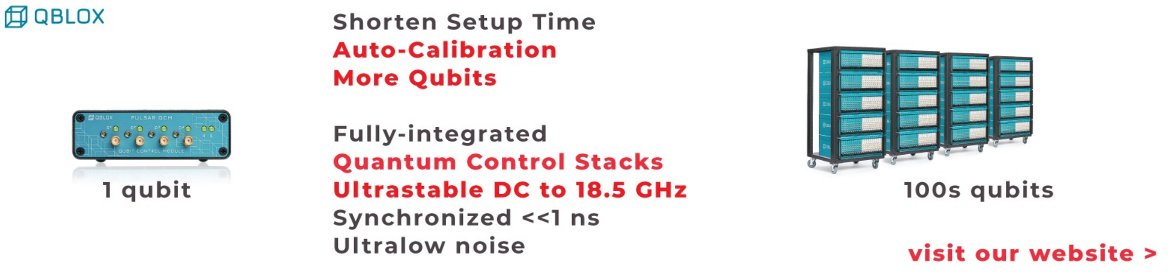

Raman analysis of the configurational disorder in $Al_xGa_{1-x}N$ films

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Raman analysis of the $E2$ mode of $Al_xGa_{1-x}N$ in the composition range $0 \leqslant x \leqslant 1$ is presented. The line shape was observed to exhibit a significant asymmetry and broadening toward the high energy range. The spatial correlation model is discussed, and is shown to account for the line shape. The model calculations also indicate the lack of a long-range order in the chemical vapor deposition alloys. These results were confirmed by x-ray scattering: the relative intensity of the superlattice line was found to be negligible. The line broadening of the $E2$ mode was found to exhibit a maximum at a composition $x \cong 0.5$ indicative of a random disordered alloy system. © *1997 American Institute of Physics.* [S0003-6951(97)04041-2]

The realization of achieving high quality $Al_xGa_{1-x}N$ films has prompted an intensive investigation concerning device fabrication and material and device properties. Raman spectroscopy has been proven in the past to be a powerful method in studying alloy systems among which are $Al_xGa_{1-x}As$, $In_xGa_{1-x}As$, $Ca_xSr_{1-x}F_2$, $ZnS_{1-x}Se_x$, and many more.[1–5] Raman scattering from a perfect crystal, which consists of a lattice with translational symmetry, involves phonons with a wave vector $q \cong 0$ near the Brillouin zone (BZ) center.[6] The alloying may destroy the configurational translational symmetry, and the phonons of $q \geqslant 0$ may be allowed to participate in the Raman scattering. As a result the Raman line shape changes, and an investigation of the line characteristics may yield valuable information on the microstructure state of the alloy.

In this letter we present for the first time observations and analytical study of an asymmetric $E2$ Raman line shape of $Al_xGa_{1-x}N$ films. The asymmetry of the line is shown to agree with the spatial correlation model which is based on the relaxation of the $q \cong 0$ selection rules due to the alloying. The calculations indicated that the $Al_xGa_{1-x}N$ lattice lacks a long-range order, a result which was confirmed by x-ray diffraction (XRD): the superlattice diffraction line was found to exhibit a very weak relative intensity. Moreover, the functional behavior of the $E2$ linewidth with respect to the composition x in the range 0–1 indicated a random distribution of the alloy constituents with maximum disorder at composition $x \cong 0.5$.

Raman spectra were acquired in a backscattering geometry in which the $E2$ and the $A1$(LO) are the allowed Raman modes from the c face of the Wurtzite (WZ) structure.[7] Unlike the nonpolar $E2$ mode, the $A1$(LO) mode possesses an electric field which interacts with that produced by the free carrier waves known as plasmons. For samples with a sufficiently high free carrier concentration, this phonon–plasmon interaction affects the $A1$(LO) Raman line shape significantly and results in a Raman signal with very weak intensity.[8] The free carrier concentration in the samples studied here, as measured via the Hall effect, is relatively high (on the order of $5 \times 10^{17}/cm^3$) and as a result the $A1$(LO) mode is not detectable in the Raman spectra. The lack of the electric field interaction makes the $E2$ mode ideal for the present study. Future investigations may address the line shape of the $A1$(LO) mode.

In the experiments the 488 nm line of an Ar^+ ion laser was utilized and the data were acquired at sample temperatures of 300 and at 10 K. The experimental error in the linewidth and peak position measurements is ± 1.5 and 0.5 cm^{-1}, respectively. The $Al_xGa_{1-x}N$ films were grown via the organometallic chemical vapor deposition (OMCVD) method at ~1100 °C on $6H$-SiC(0001) substrates with a 1000 Å AlN buffer layer.[9] The thickness of the films is ~2 μm and the composition, x, which was determined via Rutherford backscattering (RBS), energy dispersive x-ray (EDX), and Auger spectroscopy is: 0.06, 0.12, 0.22, 0.32, and 0.70. The data points for $x=0$ and $x=1$ were obtained from GaN film and AlN crystallite,[10] respectively.

Figure 1 shows the room-temperature Raman spectra of the $E2$ line from $Al_xGa_{1-x}N$ films of compositions 0.06, 0.12, 0.22, and 0.70, which exhibit linewidths of 8, 13, 16, and 19 cm^{-1}, respectively. As depicted in the figure, the spectral line shape for films of $x > 0.06$ exhibit 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 ($q \cong 0$) mode which lies in the same frequency range as the investigated line, and broadening due to activation of a collective of modes of wave vectors $q \geqslant 0$. The last two broadening mechanisms result from the elimination of the translational symmetry of the lattice due to alloying.

To investigate the thermal contribution to the line broadening, Raman spectra were acquired at $T=10$ K, and no significant change was observed between the shapes and linewidths of the room and cold temperature spectra. Thus the linewidth in our sample is not strongly affected by temperature. The only effect of the low temperature is the shifting of the peak position by ~2 cm^{-1} toward the high frequency, which was also previously observed in GaN films[8]

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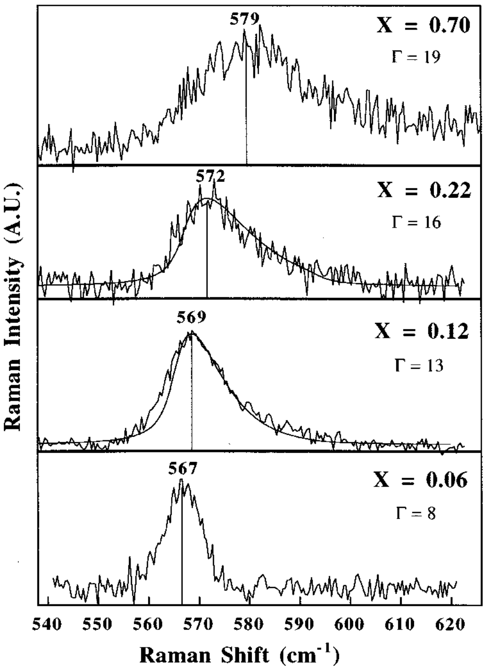

FIG. 1. The RT Raman spectra of the $E2$ mode of $Al_xGa_{1-x}N$ films of composition $x=0.06$, 0.12, 0.22, and 0.70. The respective linewidths are: 8, 13, 16, and 19 cm^{-1}, and peak positions at: 567, 569, 572, 579 cm^{-1}. The solid lines superimposed on the spectra of films: $x=0.12$ and 0.22 were calculated from the spatial correlation model presented in Eq. (1).

and crystals[11] and was attributed there to the thermal contraction of the bonding.

The second possible mechanism is the activation of a $q \cong 0$ symmetry forbidden mode which might be convoluted with the $E2$ line and cause the asymmetric broadening. However, the only mode in the frequency range of the $E2$ line that is forbidden in the backscattering geometry is the $A1(\mathrm{TO})$ mode of GaN at ~560 cm^{-1},[7] which lies at a lower frequency.

A more plausible mechanism to account for the high frequency asymmetric linewidth in our Raman spectra is the spatial correlation model, also known as the confinement model. The model was developed to explain the asymmetry line in BN[12] and Si[13] and has been successfully applied to quantify the line shape behavior of $Ga_{1-x}Al_xAs$ and $Ga_{1-x}In_xAs$ alloy systems.[1] The foundation of the model lies in the wave vector uncertainty: $\Delta q = 2\pi/L$, where Δq is the phonon wave vector range, L is a spatial dimension into which the phonon is confined, and q is related to the Raman frequency ω via the phonon dispersion relation $\omega(q)$. The size of L in an alloy system may be viewed as the average size of the ordered domains which are embedded in the configurational-disordered matrix. According to the model, as L gets smaller Δq becomes larger: a wider range of frequencies are allowed to participate in the Raman scattering, and as a result the Raman line shape exhibits a change. The line shape change depends on the phonon dispersion curve $\omega(q)$; for a curve of negative slope the line asymmetry is toward lower frequencies and for a positive slope the asymmetry is toward higher frequencies. The peak position also shifts accordingly. However, the position is a function of the alloy mode as well: an alloy can be categorized as being a one- or two-mode type[14,15] and the behavior of the peak position depends on the type. The deconvolution of the peak position is left to a future investigation; at present we address merely the origin of the asymmetric line shape and line broadening.

The Raman intensity $I(\omega)$ for the spatial correlation model may be expressed as[1,12,13]

$$I(\omega) \propto \int \exp\left(\frac{-q^2L^2}{4}\right) \frac{d^3q}{[\omega-\omega(q)]^2+(\Gamma_0/2)^2}, \qquad (1)$$

where q is in units of $2\pi/a$, a is the lattice constant, and Γ_0 is the linewidth of the material of composition $x=0$ which is GaN in this study. Our GaN films exhibit linewidth in the range 3–5 cm^{-1} depending on the film quality.[8] For the calculations we used the upper range value to account for the stress in the alloy which was inferred from the appearance of cracks in the films. In the calculation we assumed a spherical correlation domain and BZ.

To evaluate Eq. (1) we fitted the phonon dispersion curves, which have been calculated by Azuhata *et al.*,[16] in the vicinity of the BZ center. In their calculations the $E2$ mode along the Δ direction exhibits a doubly degenerate behavior and is a weak function of q, thus having no effect on the line broadening mechanism. In contrast, the $E2$ curves along the Σ and T directions both split into a lower and an upper branch, where the former is a decreasing function of q and the latter is an increasing function: these curves are expected to influence the Raman line shape. Our calculations of Eq. (1) best concur with the phonon dispersion curve of the form: $\omega(q)=A+Bq^2$ (in units of cm^{-1} and with $A=568$ and $B=100$), which is the approximated behavior of the upper branch of the Σ and T curves in the vicinity of the zone center. However, when we included the contribution to the line shape arising from the lower branches of the dispersion curves the fit was not ideal. Similar behavior has been previously observed in the calculation of BN line shape.[12] The reason for the dominance effect of the upper branches in our calculations is under investigation.

The calculated lines and the Raman data for samples of composition 0.12 and 0.22 are presented in Fig. 1. As depicted in the figure the asymmetric Raman data concur with the spatial correlation model, where the small deviation ~560 cm^{-1} may be attributed to the activated $A1(\mathrm{LO})$ mode. The ordered domain size, L, was determined from our calculations to be ~25–35 Å; a relatively small value suggesting the lack of a long-range order in the alloy system. In order to further investigate this hypothesis a film of composition $x=0.22$ was characterized by XRD: the scan is presented in Fig. 2. The figure shows the diffraction peak of the (0002) planes of the AlGaN (superimposed is also the SiC substrate peak) and the inset presents the weak (0001) diffraction peak. The (0001) is a forbidden reflection in the WZ structure and appears as a superlattice line only when lattice ordering exists;[17] the intensity ratio (0001)/(0002) is a measure of the extent of the order.[18] $Al_xGa_{1-x}N$ films which were grown by molecular beam epitaxy have been reported by Korakakis *et al.*[17] to exhibit a long range order; the intensity ratio of their XRD lines is ~0.05 in contrast to our much smaller intensity ratio of ~0.002. Thus the XRD confirms

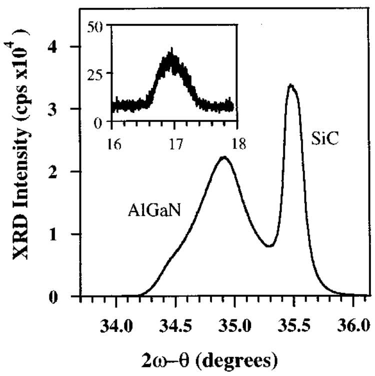

FIG. 2. The (0002) x-ray diffraction of $Al_{0.22}Ga_{0.78}N$; the scan displays the SiC substrate peak. The inset to the figure shows the very weak (0001) superlattice line.

the Raman analysis, indicating that the alloys in this study do not exhibit significant long-range ordering.

More insight into the alloy microstructure may be obtained from the Raman linewidth behavior. Figure 3 presents the Raman linewidths of the $E2$ mode as a function of the composition. The linewidth behavior follows a pattern which exhibits a maximum at composition $x \simeq 0.5$, a value at which a maximum disorder should be expected in a random system. The solid line in the figure was calculated (in arbitrary units) using the relation for the entropy of mixing which is a measure of the configurational disorder in a random alloy.[19] Thus our data suggest that the distribution of the alloy constituents for the most part is random. The issue of randomness in $A_xB_{1-x}C$ alloys has been previously addressed and it was suggested that the anions, C, are periodically distributed in their sublattice sites, while the cations, A and B, are randomly distributed in the other sublattice sites.[2,20] However, achieving an ordered alloy in some families of ternary tetrahedral semiconductors has been demonstrated to be a function of the growth temperature;[20] the conditions for the ordered state in the $Al_xGa_{1-x}N$ system have yet to be explored.

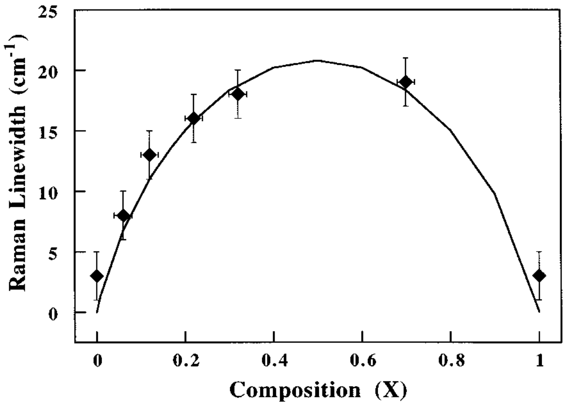

FIG. 3. The $E2$ Raman linewidth as a function of composition (dots). The solid line is obtained from calculations of the entropy of mixing of an alloy system (in arbitrary units).

To conclude, the asymmetric behavior of the $E2$ Raman linewidth of $Al_xGa_{1-x}N$ alloys was attributed to the activation of phonons of $q \geqslant 0$ arising from the disordered state of the alloys. X-ray diffraction supports the finding; the superlattice relative line intensity is weak. The line broadening of the $E2$ Raman mode exhibits a maximum at composition $x \simeq 0.5$, which is consistent with a random distributed system.

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