Raman line-shape analysis of random and spontaneously ordered $GaInP_2$ alloy

K. Sinha, A. Mascarenhas, G. S. Horner, K. A. Bertness, Sarah R. Kurtz, and J. M. Olson
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401
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We have measured the temperature dependence of the Raman frequency and linewidth of the GaP-like LO phonon of random and spontaneously ordered $GaInP_2$ alloys. The width of the asymmetric Raman band is strongly influenced by disorder and the anharmonicity of the lattice. The half-width towards the high-energy side of the Raman band of the GaP-like phonon is independent of temperature, while the half-width on the low-energy side does depend on temperature. Though no obvious differences are observed in the temperature dependence of the Raman spectra of the random and the ordered alloys, the GaP-like Raman band of the ordered samples narrows for incident photon energies near the fundamental gap of the alloy. We attribute the narrowing of the Raman band to the inhomogeneities in the material caused by the existence of a statistical distribution of partially ordered domains with different order parameters η. From the observed width of the dispersion of the Raman linewidth as a function of incident photon energies under resonance conditions, it is concluded that samples grown at higher temperatures possess a narrower distribution of domains.

I. INTRODUCTION

$GaInP_2$ alloys have attracted considerable attention due to their potential application for various photonic[1] and high-efficiency photovoltaic devices.[2] For a judicious choice of growth conditions these alloys exhibit a spontaneous formation of a monolayer superlattice along the $\langle 111 \rangle$ B directions.[3] The electronic properties of the spontaneously ordered material are markedly different from that of the random alloy. In particular, the spontaneously ordered materials show a reduction of the fundamental band gap and a splitting of the otherwise degenerate valence bands of the random alloy. These changes in the electronic structure have been explained on the basis of doubling of the unit cell and the reduced symmetry of the Cu-Pt structure.[4] Though the modifications to the electronic structure of the ordered $GaInP_2$ have been studied extensively,[5-9] the vibrational properties of these materials have received relatively little attention. In a previous paper, we have demonstrated the sensitivity of the resonance Raman technique to the changes in the band structure of the spontaneously ordered $GaInP_2$ alloy.[10] In this paper, we examine the temperature dependence of the GaP-like LO phonon and the changes in the Raman line shape under resonance with the E_0 gap for both the ordered and random alloys. It is found that the temperature dependence of the linewidth of the Raman band of the GaP-like phonon has considerable contribution from both the effects of disorder and lattice anharmonicity. The sensitivity of Raman scattering to local atomic arrangement in alloys has been exploited in the past to study clustering effects[11] and variations in composition from a nominal value[12] under resonant conditions. The inhomogeneity of the electronic properties of semiconductors manifests itself in the distortion of the Raman line shape for incident photon energies in the vicinity of an allowed optical transition for the material.[13] The Raman line shape of the ordered $GaInP_2$ epilayers exhibits interesting changes for excitation of the samples with photon energies close to the fundamental gap of the material. These changes are related to the fact that the microstructure of the spontaneously ordered samples contains a statistical distribution of domains with different order parameters η.[14,15]

II. EXPERIMENTAL DETAILS

The $GaInP_2$ samples used in this study were prepared by organometallic vapor-phase epitaxy technique. 3000-Å-thick $Ga_{0.52}In_{0.48}P$ epilayers were grown on (001) GaAs substrates, misoriented by 2° towards the $[1\bar{1}1]B$ direction, at substrate temperatures ranging from 630°–750 °C. The details of the growth process have been described elsewhere.[14] The electronic properties of these samples have been extensively studied by photoluminescence, photoluminescence excitation[16] (PLE), and piezomodulated reflectivity techniques.[17] The sample grown at 670 °C shows the largest reduction in the band gap with respect to the random alloy. The epilayer growth at 750 °C is the least ordered, while samples grown at other temperatures exhibit intermediate degrees of ordering. Raman measurements were performed using either the 5145-Å line of an Ar^+-ion laser or emission from a DCM special dye laser. The scattered light was dispersed either by a 0.85-m double monochromator equipped with a photon counting system or a 0.6-m triple spectrometer equipped with a charge-coupled device detector. The resolution of the spectrometers was set at 2 cm^{-1}. The low-temperature measurements were performed using a continuous-flow helium cryostat.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1(a) shows the Raman spectra from samples grown at 750 °C and 670 °C under cross-polarization conditions measured at 15 K. The Raman spectrum of

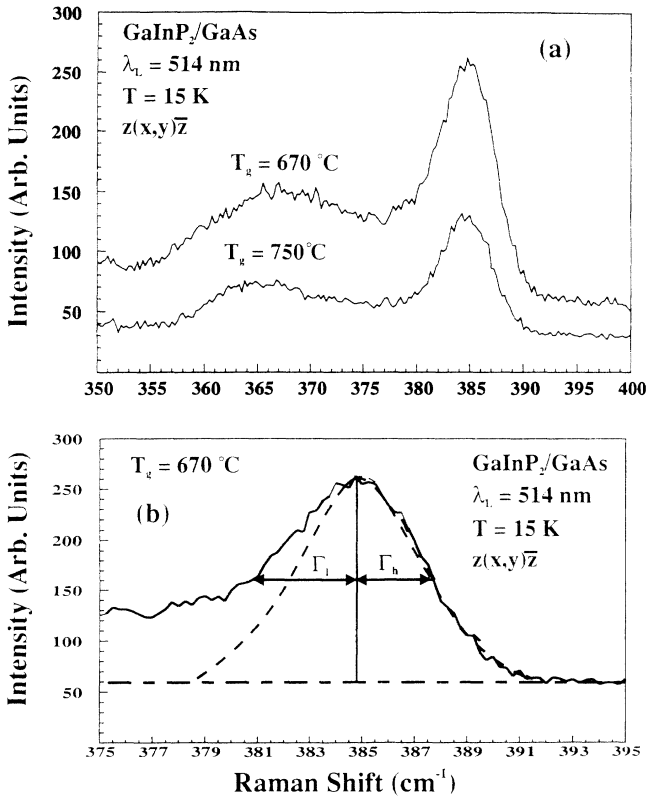

FIG. 1. (a) Raman spectra of the random [T_g=750 °C, E_g(RT)=1.88 eV] and the ordered [T_g=670 °C, E_g(RT)=1.83 eV] $GaInP_2$ alloy measured at 15 K. (b) Expanded view of the Raman spectrum of the ordered $GaInP_2$ alloy. The broken line is a Lorentzian fit to the high-energy part of the Raman spectrum.

$GaInP_2$ alloys exhibits a modified two-mode behavior[18] and consists of a broad asymmetric GaP-like LO feature at ~385 cm^{-1}, the InP-like LO band at ~365 cm^{-1}, and a TO mode at ~340 cm^{-1} (not shown). The deviations from the zinc-blende selection rules for the Raman spectra of the ordered material have been discussed earlier.[10] No systematic variations in the phonon frequencies are observed between the ordered and the random alloys.

Figure 1(b) displays an expanded view of the GaP-like Raman band of the most ordered sample measured at 15 K. The GaP-like band is broad and asymmetric with a relatively sharp cutoff on the high-energy side and a long tail extending down to the InP-like band. The observed line shape is typical of ternary alloys[19–21] and has been described theoretically within the framework of the coherent-potential approximation.[22] The observed 7 cm^{-1} full width at half maxima (FWHM) of the GaP-like band is much larger than the FWHM of 0.36 cm^{-1} observed for the binary GaP.[23] The large broadening observed in the Raman spectra may arise either from the anharmonicity in the lattice or be due to alloy disorder produced by fluctuations in the cation-site occupancy. Since the anharmonic contribution to the linewidth at 15 K is small, it appears that the major contribution to the linewidth arises from disorder effects.

Due to the presence of translational symmetry in a perfect crystal, only the $k \sim 0$ phonons are accessible to Raman scattering. The presence of cation fluctuations in the ternary alloy leads to the breakdown of the momentum-conservation rule and phonons throughout the Brillouin zone can become Raman active. The peak in the Raman spectrum in Fig. 1(b) arises from the highest-frequency, zone-center GaP-like LO phonon in the material. To study the temperature dependence of the Raman spectra, we extract the peak position and the width of the highest-phonon by fitting only the high-energy part of the Raman band with a Lorentzian.

An example of such a fit is also shown in Fig. 1(b). A reasonably good fit is obtained for the high-energy side of the Raman spectrum. A half-width at half maximum of 2.5 cm^{-1} is obtained from the fitting procedure. This width is much larger than the homogeneous broadening caused purely by lattice anharmonic effects in typical III-V binaries. The Raman FWHM of single-crystal GaP is 0.36 cm^{-1}.[23] The presence of cation fluctuations on the group-III sublattice and additional scattering at the boundaries of the ordered domains in Cu-Pt ordered alloys would lead to a broad Raman peak. The broadening on the low-energy tail of the experimental data that is not accounted for by the fit is attributed to scattering from phonons, which are not exactly at the center of the Brillouin zone.

Figure 2(a) shows the temperature dependence of the highest-energy GaP-like phonon frequency of the most ordered and the random alloy. A rigorous description of the temperature dependence of phonon frequencies requires a knowledge of the anharmonic potential and the phonon self-energy.[24] Since these quantities are not available in the literature, we describe the temperature dependence of the phonon frequency by assuming a decay process of the LO phonons into two phonons of equal frequencies. The temperature dependence of the shift in Raman frequency can be described by[25]

$$\Delta\omega(T) = AT + B\left[1+\frac{2}{e^{x}-1}\right], \tag{1}$$

where the first term on the right-hand side is the contribution to the shift from the lattice-expansion effect, the constant B determines the cubic contribution to the decay process, and $x=\hbar\omega_0/2k_BT$ where ω_0 is the $T=0$ K phonon frequency. The values of A, B, and ω_0 obtained from the fit are 0.0044 cm^{-1} K^{-1}, 1.97 and 386 cm^{-1}, respectively, for the ordered epilayer.

The temperature dependence of the width of the highest-energy GaP-like Raman band of the most ordered sample is plotted in Fig. 2(b). The data are a good representation of other $GaInP_2$ alloy samples as well. The width of the Raman band is independent of temperature. This indicates that the broadening of the Raman feature corresponding to the GaP-like phonon is strongly dominated by the inhomogeneity in the film. For comparison, the temperature dependence of the Raman linewidth of the LO phonon of single-crystal GaP is also plotted in Fig. 2(b). The behavior of the LO phonon in this case can be described well by homogeneous broaden-

ing caused by the effects of lattice anharmonicity alone.[23] The dependence of the Raman linewidth of the GaP-like phonon of the alloy on temperature is in contrast with the dependence of the GaAs-like phonon in $Al_xGa_{1-x}As$ alloys, where the width of the Raman linewidth is only weakly affected by the disorder on the cation sublattice.[19]

Figure 3 demonstrates the temperature dependence of the ratio of the half-widths of the low-energy to the high-energy side, Γ_l/Γ_h, of the Raman spectra for the most ordered and the random alloy. It is observed that the asymmetry is a strong function of temperature. Since the low-energy tail of the Raman band arises from scattering by phonons that originate away from the zone center and the width of the Raman feature arising from the highest-energy GaP-like phonon is independent of temperature, the increase in asymmetry can be attributed to the anharmonicity of the phonons, which are away from the Γ point in the Brillouin zone. This behavior is again in contrast to the situation observed in $Al_xGa_{1-x}As$ alloys where the asymmetry of the GaAs-like Raman band is only weakly affected by tempera-

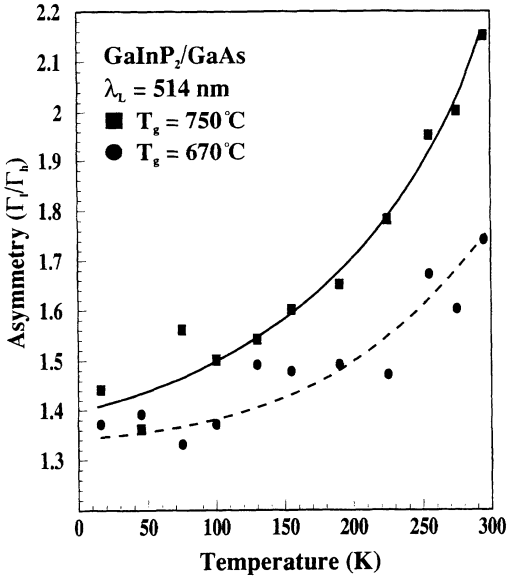

FIG. 3. Temperature dependence of the asymmetry, Γ_l/Γ_h, of the Raman spectra for the ordered (■) and the random (●) $GaInP_2$ alloy. The lines are meant as an aid to guide the eye.

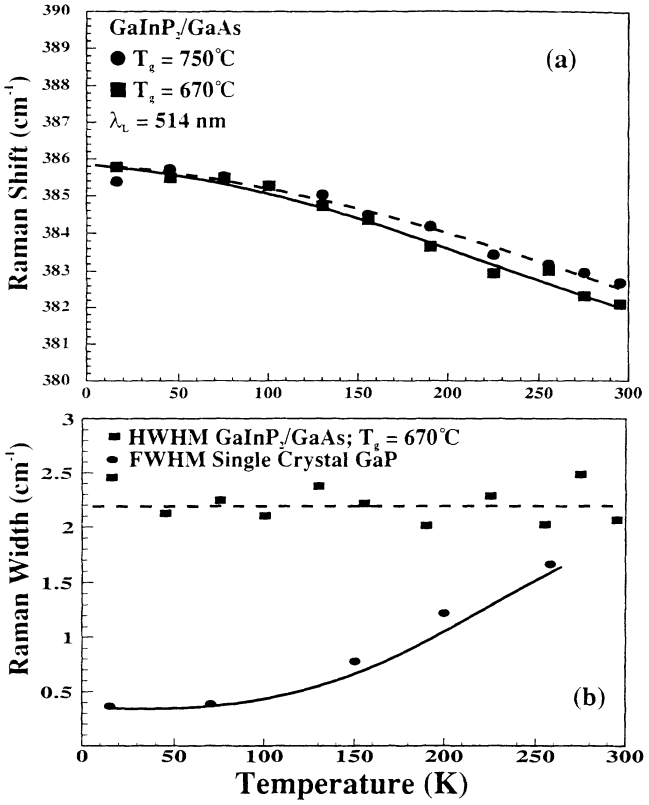

FIG. 2. (a) Temperature dependence of the Raman shift of the GaP-like LO phonon of the ordered and the random alloy. The solid and broken lines represent the best fit to the data assuming cubic contribution of the anharmonicity to the decay process. (b) Temperature dependence of the Raman width of the GaP-like LO phonon for the alloy (■) and single crystal GaP (●). The broken line is meant as an aid to guide the eye, while the solid line is the fit to the experimental data assuming cubic anharmonicity. The data for single crystal GaP are taken from Ref. 23.

ture.[19] A possible explanation for the strong dependence of the asymmetry of the Raman line shape on temperature in the case of $GaInP_2$ alloys may lie in the fact that the InP-like LO phonon branch is situated below the GaP-like phonon branch, and hence gives rise to additional decay channels for the GaP-like phonons.

Though the temperature dependence of the Raman linewidths and shifts show no significant variation between the ordered and the random alloy, significant differences are observed in the linewidth dependence on the incident photon energy in the vicinity of the fundamental gap for the two cases. Figures 4(a)–4(c) show the behavior of the Raman linewidth Γ_h of the highest-energy GaP-like phonon as a function of the laser excitation energy for $GaInP_2$ samples exhibiting different degrees of ordering. The incident light was polarized along the [110] direction to ensure the enhanced coupling with the E_0 gap of the material.[10] Since the low-energy tail of the band arises from the superposition of modes away from the zone center, we choose to study the dependence of the half-width of the Raman band towards the high-energy side Γ_h. For the nearly random alloy, no variations in the Raman half-width are observed as the excitation energy is varied across the fundamental gap of the sample. For the samples exhibiting various degrees of ordering, the half-width shows a decrease in the vicinity of the E_0 gap of the material. It should also be noted that the Γ_h for the ordered alloys is greater than the Raman width of the nearly random sample. This increase, however, is not surprising if one considers that additional scattering from domain boundaries in the ordered material will give rise to larger linewidth as compared to scattering from alloy fluctuations alone. An accurate determination of the position of the Raman band near resonance is hindered by the presence of strong lumines-

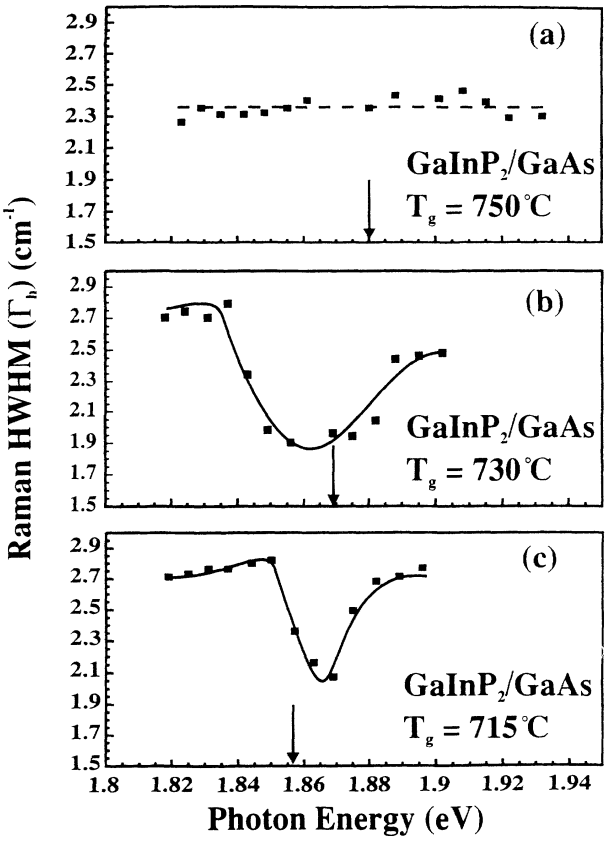

FIG. 4. Variation of the high-energy Raman half-width Γ_h with incident photon energy in the vicinity of the fundamental gap of the $GaInP_2$ alloy for epilayers grown at (a) 750 °C, (b) 730 °C, and (c) 715 °C. The lines are meant as an aid to guide the eye. The arrows indicate the measured band gap of the samples.

cence from both the epilayer and the GaAs substrate. No systematic shifts in the position of the GaP-like Raman band as a function of excitation energy could be detected within ± 1 cm^{-1}. Thus, any dependence of the position of the GaP-like Raman band on the degree of ordering is expected to be small.

The reduction in the Raman half-width Γ_h of the spontaneously ordered alloys for excitation close to the fundamental gap of the material can be explained if one remembers that the microstructure of the ordered materials consists of an inhomogeneous distribution of partially ordered domains with different degrees of ordering. The Raman spectra of such materials is a superposition of the Raman spectrum of phonons originating from different domains within the sample volume. As the incident photon energy is tuned to the band gap of a particular domain, the contribution to the Raman cross section from that region of the material is resonantly enhanced. Such an enhancement will result in reduction of the overall width of the Raman band. Of course, no narrowing of the Raman line shape is expected for alloys that are uniformly ordered or disordered, since only a single optical transition corresponding to a unique order parameter would be expected for such materials. It should also be noted that for photon energies above the gap of the ordered material, the half-width Γ_h, is slightly lower than the observed width of the Raman band for excitation below the gap. The reduction in the half-width of the Raman band for excitation above the gap could arise due to either a resonance with the outgoing channel or a weak coupling with the crystal-field splitoff band.[10]

The width of the observed dispersion of Γ_h in Fig. 4 can be used as a convenient tool to measure the degree of uniformity of the ordered materials. This width is plotted in Fig. 5(a) as a function of growth temperature. A narrower width is indicative of greater uniformity in the material. It is observed that, in general, alloy samples grown at temperatures close to, or greater than 670 °C, exhibits a greater degree of homogeneity than the samples grown at lower temperatures. Our results support transmission electron-diffraction data on ordered $GaInP_2$, which show sharp superlattice spots for samples grown at higher temperatures and streaky images for epilayers grown at low-growth temperatures,[26,27] indicating a greater degree of homogeneity in epilayers prepared at higher temperature.

The absorption edge measured by PLE spectroscopy on the set of samples under study showed an interesting correlation between the band-gap reduction and the 10-90 rise of PLE edge.[16] For the nearly random alloy, the absorption edge displays a sharp rise with an excitonic signature, while the slope softens for samples with

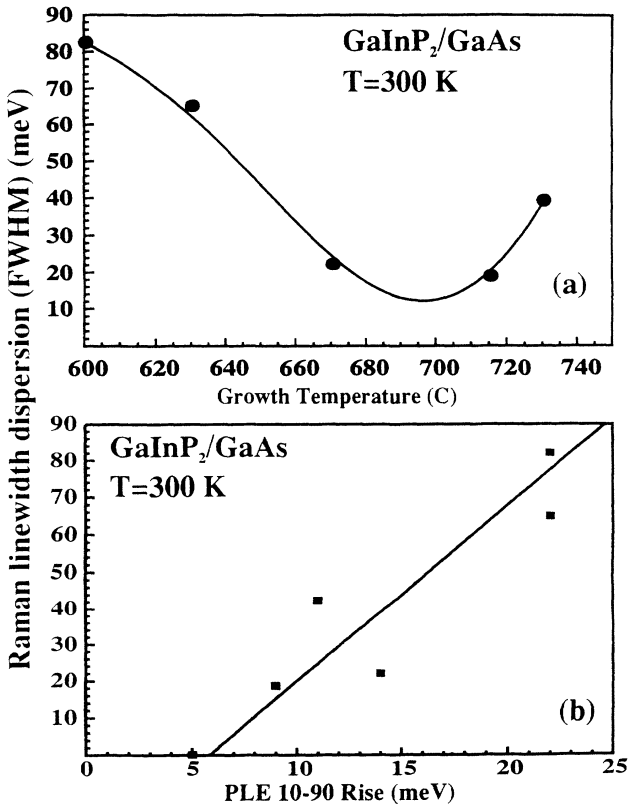

FIG. 5. (a) The dependence of the full width at half minima of the dispersion observed in Fig. 4 as a function of growth temperature. (b) The FWHM dependence of the dispersion of Fig. 4 on the measured PLE 10-90 rise of the epilayers.

different degrees of ordering. The softening of the slope in the ordered materials was attributed to the presence of a distribution of gaps within the probe volume. Since the width of the dispersion of Γ_h with respect to the incident photon energy is also a measure of the same distribution, it is of interest to compare the PLE 10-90 rise with the corresponding Raman data. Such a comparison is made in Fig. 5(b). A positive correlation is observed between the PLE 10-90 rise and the width of the dispersion of Γ_h with incident photon energy. The Raman results thus provide additional support to the interpretation of the PLE data.

In conclusion, a comprehensive study of the GaP-like optical phonon in random and spontaneously ordered $GaInP_2$ alloy has been performed. The temperature dependence of the Raman linewidth indicates the strong influence of cation fluctuations and phonon scattering at the boundaries of ordered domains in these materials. The dependence of the asymmetry of the Raman line shape on temperature is produced by the influence of the anharmonicity of the lattice on the phonons, which lie away from the zone center. Though the temperature dependence of the Raman spectra of the random and the ordered alloys does not show any obvious differences, significant changes are observed in the shape of the Raman band of the ordered materials for excitation close to the fundamental gap of the material. The observed narrowing of the GaP-like Raman band in spontaneously ordered samples in the vicinity of the fundamental gap has been attributed to the presence of a statistical distribution of partially ordered domains in these materials. The narrowing of the Raman band provides an effective probe to measure the degree of uniformity of ordering in these alloys. The Raman data also support the interpretation for the observed softening of the PLE edge in the ordered $GaInP_2$ alloys.

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