Raman scattering reveals strong LO-phonon-hole-plasmon coupling in *nominally undoped* GaAsBi: optical determination of carrier concentration

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Abstract: We report room-temperature Raman scattering studies of *nominally undoped* (100) $GaAs_{1-x}Bi_x$ epitaxial layers exhibiting Bi-induced (*p*-type) longitudinal-optical-plasmon-coupled (LOPC) modes for $0.018 \leq x \leq 0.048$. Redshifts in the GaAs-like optical modes due to alloying are evaluated and are paralleled by strong damping of the LOPC. The relative integrated Raman intensities of LO(Γ) and LOPC $A_{\mathrm{LO}}/A_{\mathrm{LOPC}}$ are characteristic of heavily doped *p*-GaAs, with a remarkable near total screening of the LO(Γ) phonon ($A_{\mathrm{LO}}/A_{\mathrm{LOPC}} \to 0$) for larger Bi concentrations. A method of spectral analysis is set out which yields estimates of hole concentrations in excess of $5\times10^{17}\mathrm{cm}^{-3}$ and correlates with the Bi molar fraction. These findings are in general agreement with recent electrical transport measurements performed on the alloy, and while the absolute size of the hole concentrations differ, likely origins for the discrepancy are discussed. We conclude that the damped LO-phonon-hole-plasmon coupling phenomena plays a dominant role in Raman scattering from unpassivated *nominally undoped* GaAsBi.

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1. Introduction

Dilute incorporation of large Bi atoms into GaAs induces changes to the physical and electronic properties of the host [1–4]. Bi induces a (temperature-independent) strong decrease in the bandgap energy and a giant increase in the spin-orbit splitting [5–7]. Thus GaAsBi is an emerging material receiving considerable attention for scientific and technological interests, with applications spanning IR optics, optoelectronics [8], and terahertz [9]. These attractive properties are mainly related to the large disparity in atomic size and electronegativity between Bi and As, and to the relativistic corrections induced by the bismuth. Recently, Nargelas *et al.* [10] showed alloying *nominally undoped* GaAs with group V Bi counterintuitively introduces p-type carriers: holes thermally excited from Bi-induced acceptor levels lying 26.8 meV above the valence band edge [11]. Pettinari *et al.* [12] revealed – through electrical transport measurements – that the hole concentration rises with x up to $p = 2.4 \times 10^{17}\,\mathrm{cm}^{-3}$ at $x = 10.6\%$. They [13] further demonstrated that the acceptor states are passivated through hydrogen incorporation. Needless to say, within the context of current research on GaAsBi applications, these recent results have large implications for future technological interests.

In polar semiconductors like GaAs, LO(Γ) phonons couple strongly with the collective oscillations of the free-carrier system (plasmons). The extent of coupling, or mixing, is greatest when the two modes are of comparable energies and depends strongly on carrier concentration. For n-GaAs this results in two LO-plasmon-coupled (LOPC) branches, L_+(upper) and L_-(lower), for a given plasma frequency ω_p. However, due to large carrier damping, only one LOPC mode is generally observed in p-GaAs [14]. Figure 1 shows the uncoupled and coupled modes with the single observable damped LOPC mode for p-GaAs near the LO and TO frequencies with increasing hole concentration [15]. Given the native acceptors in GaAsBi, one would expect damped LOPC modes in the Raman spectra (RS) for sufficiently large carrier concentrations. An early Raman study of $\mathrm{GaAs}_{1-x}\mathrm{Bi}_x$ uncovered, along with new Ga-Bi center optical modes, damped LOPC modes for $x \leq 2.4\%$ [16]. The free charge carriers were attributed to a carbon contamination and the concentration estimated to be greater than $10^{18}\,\mathrm{cm}^{-3}$ [16].

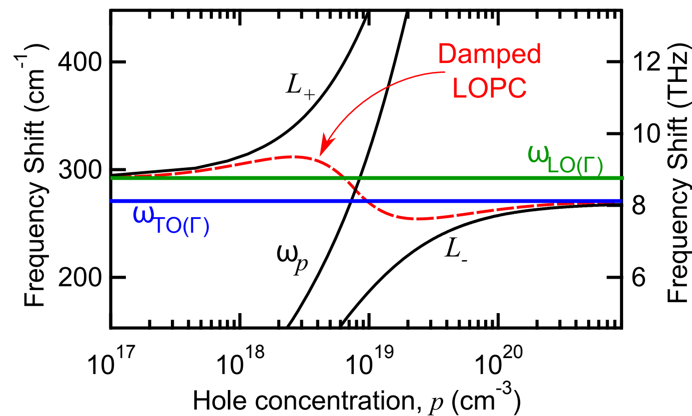

Fig. 1. Predicted [17] frequencies of the coupled modes (L_+ and L_-) and the plasma mode (ω_p) as a function of hole concentration. The dashed line shows the general behavior of the single damped LOPC mode observed in p-GaAs.

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The determination of native hole concentrations in dilute and unpassivated GaAsBi is very important for device fabrication. The Hall effect is typically the method used for measuring the carrier concentration in semiconductors, which requires fabrication of ohmic contacts. In this paper, Raman scattering from the LO-phonon-hole-plasmon coupled mode is investigated in *nominally undoped* $GaAs_{1-x}Bi_x$ for $x \leq 0.048$. From a detailed examination of Raman features, our spectral analysis reveals that hole concentrations exceed $5 \times 10^{17} cm^{-3}$ and correlate with the Bi molar fraction. Interestingly, samples with larger Bi contents display significant or near total screening of the LO(Γ) band. While the absolute size of the hole concentrations determined here diverge from the transport measurements of Pettinari *et al.* [12], likely origins for the discrepancy are discussed.

2. Experiment

2.1. Sample details

Our (100) $GaAs_{1-x}Bi_x$ samples are grown by molecular-beam epitaxy for Bi concentrations $0.018 \leq x \leq 0.0478$. Two sets of samples were grown, denoted A and B, having nominal epilayer thicknesses 1 μm and 0.3 μm, respectively. Bi content was found by combining X-ray diffraction [18], energy-dispersive X-ray spectroscopy, and photoluminescence [19]. More details of the samples are given elsewhere [20].

2.2. Experimental setup

Room-temperature RS were acquired in a quasi-backscattering configuration on the (100) surface using a Jobin-Yvon HR800 integrated micro-Raman setup with Olympus 100$\times$ microscope, 20 mW HeNe laser, working at 633 nm, and air-cooled CCD detector. Dispersion was by a 1800 g/mm diffraction grating (spectral resolution 0.2 cm^{-1}). Correct instrument calibration was verified by checking the position of the Si band at $\pm$ 520.7 cm^{-1}. With the addition of two linear polarizers, measurements were performed in experimental configuration described as $-c(\vec{E}_{incident}, \vec{E}_{scattered})c$. For our samples, the epilayer thicknesses are large compared to the optical absorption depth $d_{opt} = 1/(2\alpha)$, so that there is negligible signal from the substrate. While it is known that the incorporation of large Bi atoms into the GaAs matrix deteriorates optical quality, we observe a consistent RS lineshape from representative probing locations across all the samples studied here. Optically defective samples were omitted from the study.

3. Results and discussion

Figure 2(a) shows a typical depolarized RS of (100) $GaAs_{1-x}Bi_x$, for $x = 0.043$, showing a two-mode behavior (GaBi-, GaAs-like optical modes) with small disorder-activated GaAs-like signatures weakly contributing to the background [18]. Figure 2(b) expands the RS over the GaAs-like TO and LO frequency range for four different quasi-backscattering geometries. Here z and $-z$ represent the incident and scattered photon directions (001) and (00$\bar{1}$), while $x = (100)$, $y = (010)$, $X = (1\bar{1}0)$, and $Y = (110)$. According to the Raman selection rules (zincblende, T_d site symmetry), the LO(Γ) phonon is allowed for $-z(Y,Y)z$ and $-z(x,y)z$ but forbidden in $-z(Y,X)z$ and $-z(x,x)z$, while TO(Γ) is always forbidden. The appearance of the symmetry-forbidden TO mode (in all polarizations) can be attributed to bismuth-induced disorder in the lattice, resulting in a relaxation of the Raman selection rules. The contribution to the Raman efficiency of the coupled modes from the electro-optic mechanism is not total while the unscreened LO band is present, meaning the observed LOPC modes are phonon-like and should obey the Raman selection rules. The strong feature just below TO ($\sim$266 cm^{-1}) obeys the same Raman selection rules as the LO band and indicates a LOPC mode in heavily doped ($>10^{19}$ cm^{-3}) p-GaAs [15, 17, 21, 22]. We do not observe the L_+ branch at higher frequencies,

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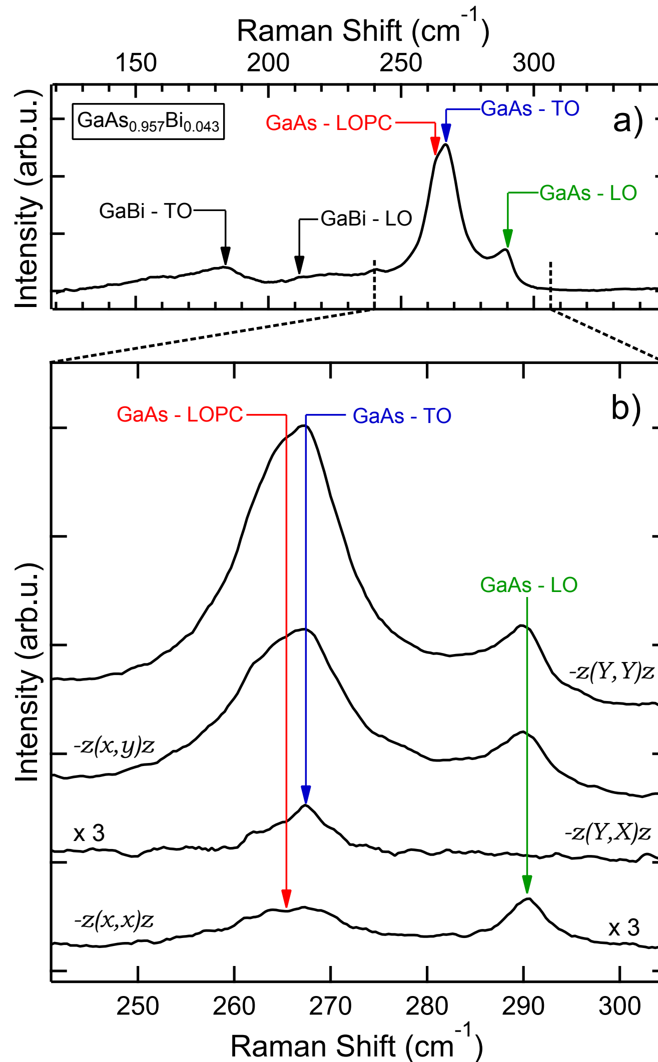

Fig. 2. RS of (100) $GaAs_{1-x}Bi_x$ for $x = 0.043$. (a) The two-mode behavior of the ternary alloy in a depolarized quasi-backscattering geometry over Raman shifts of 120–350 cm^{-1}. (b) Expanded over GaAs-like optical frequency range for different polarization configurations (offset vertically for clarity).

confirming the *p*-type nature of the free carrier present in GaAsBi. Similar RS were measured for all nine GaAsBi samples. It should be noted that while we observe weak GaBi-like center optical bands over the whole compositional range, we do not see hole plasmons interacting with the GaBi-like LO(Γ) phonon since the coupling strength is approximately proportional to the phonon content.

For RS in a $-z(Y,Y)z$ geometry, Lorentzian oscillators are assigned to each feature to deconvolute the $GaAs_{1-x}Bi_x$ Raman spectrum, as shown in Fig. 3 for x = 0, 0.018, 0.0274, 0.0301, 0.043 and 0.0478. The peak positions of TO and LO (and subsequently LOPC) are seen to linearly decrease with alloying. The peak frequency and broadening versus Bi content for all samples are summarized in Fig. 4. From the linear fit of these data, we obtain the composition

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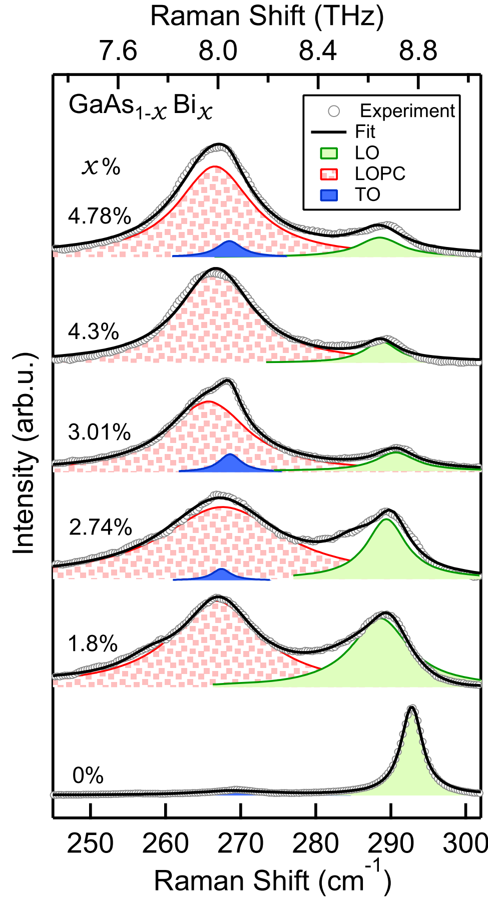

Fig. 3. Normalized RS of $GaAs_{1-x}Bi_x$ for $x = 0$, 0.018, 0.0274, 0.0301, 0.043, and 0.0478 at room temperature for 633 nm excitation in $-z(Y,Y)z$ scattering geometry. The filled areas give the contribution of distinct modes to the overall fit (solid line) of our data (open circles). For clarity, traces have been normalized and offset vertically. The vacant area corresponds to disorder activated modes.

dependence of the GaAs-like TO(Γ) and LO(Γ) modes in strained (100)-oriented $GaAs_{1-x}Bi_x$:

$$\omega_{(\mathrm{TO,LO})}(\mathrm{cm}^{-1}) = \omega^0_{(\mathrm{TO,LO})} + \Delta\omega_{(\mathrm{TO,LO})} \times x, \tag{1}$$

where the measured redshift value for the TO band is $\Delta\omega_{\mathrm{TO}} = -27(\pm 4)\ \mathrm{cm}^{-1}$ and the value for the LO phonon redshift agrees well with our previous study [18] at $\Delta\omega_{\mathrm{LO}} = -71(\pm 3)\ \mathrm{cm}^{-1}$. Figure 1 indicates that for low hole doping the LOPC mode is slightly blueshifted relative to ω_{LO} before redshifting towards ω_{TO} (crossing at $p \sim 5 \times 10^{18}\ \mathrm{cm}^{-3}$) with increasing hole concentrations and reaching ω_{TO} at higher concentrations ($p \geq 5 \times 10^{20}\ \mathrm{cm}^{-3}$). In our data, as the Bi molar fraction increases, the LOPC mode not only generally increases in intensity, but also softens well below TO for the entire compositional range studied. It is clear when comparing our data with representative p-GaAs LOPC lineshapes in the 10^{18}– $10^{20}\ \mathrm{cm}^{-3}$ doping range [15], we are well into the 'final stage' of the asymptotic approach to TO from LO. The further shift can be accounted for by the absence of lattice relaxation in the strained $GaAs_{1-x}Bi_x$ epilayers, which manifests itself through a weaker dependence on the Bi content for ω_{TO} than ω_{LO},

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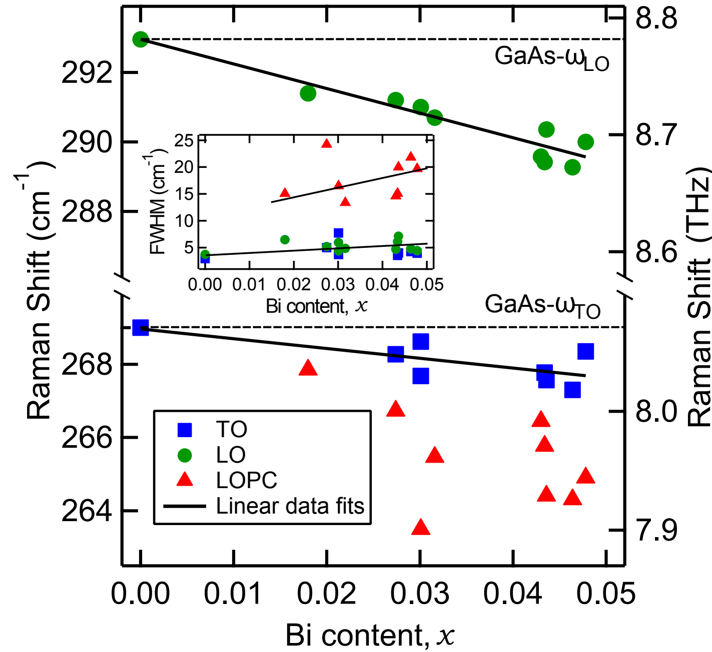

Fig. 4. Measurement of frequency shifts of the TO, LO and LOPC bands as a function of Bi fraction. Dashed lines represent the frequencies of the two center optical modes for GaAs ($x = 0$) and the inset shows the FWHM of each of the modes.

and consequently a reduction in the ionic plasma frequency associated with the LO phonon, $\Omega^2_{\mathrm{GaAs}} = (\omega^2_{\mathrm{LO}} - \omega^2_{\mathrm{TO}})$ [23].

The fact the LOPC peak frequency for our lowest Bi content is well below that expected (not measured directly for this sample) as well as only having a scattering intensity comparable to that of the LO band, suggests damping effects dominate the phonon-hole-plamson interaction in GaAsBi. The damping constant of the plasma oscillation Γ_p can be evaluated by the hole scattering rate as

$$\Gamma_p = \tau^{-1} = \frac{e}{\mu m^*}, \tag{2}$$

where e is the electrical charge, τ, μ, and m^* are the average scattering relaxation time, hole mobility, and effective mass of the free carrier, respectively. The intrinsically low hole mobility μ_h, due to large hole effective mass m^*_h, damps the coupled mode and induces broadening. The damping is more severe for GaAsBi than for GaAs since additional scattering mechanisms exist in a highly mismatched ternary alloy. Pettinari *et al.* [12] measured an order of magnitude reduction in μ_h for $\mathrm{GaAs}_{1-x}\mathrm{Bi}_x$ for $x < 6\%$ with corresponding increase in m^*_h. The FWHM of the two GaAs-like optical modes in Fig. 4 shows a similar steady increase as a result of Bi-induced disorder, while the LOPC peak broadens more rapidly. The coupled linewidth, which corresponds to mode damping, is roughly in inverse proportion to the phonon content of the mode [26]. From Fig. 1, the coupled mode should only dampen and broaden in the vicinity of ω_p crossing ω_{LO}. These data further support the notion of a large Bi dependent damping constant, however further measurements on more dilute alloys ($x \leq 0.018$) would aid comparison.

Conventional spectral analysis of the LOPC mode to study hole densities in p-type GaAs [21] assumes that the TO and LO frequencies, and other physical parameters of GaAs, do not drastically change over the doping concentrations used. The compositional redshift of the

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bands observed here introduces a problem in implementing such techniques into our analysis. However, by careful examination of the relative integrated scattering intensities of the LO and LOPC modes, we can spectroscopically estimate carrier concentrations [14].

We must first derive an expression of the Raman scattering cross section by taking into account the presence of a surface depletion region of width d [24] and adopt a simple two-layer (surface depletion layer/bulk material) model [25]. For optical penetration depths $> d$, the RS exhibits both LOPC modes from the bulk and unscreened LO phonon components from the depletion layer. The thickness of the surface depletion layer for large hole concentrations is estimated using the Schottky model

$$d = \left(\frac{2\varepsilon_0 \varepsilon_S \mathrm{V_B}}{ep} \right)^{1/2}, \tag{3}$$

where $\mathrm{V_B}$ and ε_S are the band bending and static dielectric constant, respectively. The inverse relationship of d on p implies that as hole concentrations rise the LO phonon scattering volume approaches zero. When the LOPC mode changes from phonon-like to plasmon-like the LO band is said to be totally screened. Thus the intensity of the LO phonon scattered within the depletion layer essentially depends on the size of d and the penetration depth of the probe beam; however, we assume the Raman scattering by LO phonons in the depletion layer is similar to that in a undoped crystal. Given the low Bi content of our samples, we estimate that the Raman scattering cross section of the unscreened LO mode is similar to that in pristine GaAs. Light scattering from charge density fluctuations are not considered because the intensity is estimated to be of the order of 10^{-3} less than the phonon scattering intensity in p-GaAs. Then the integrated intensity of the LO phonon band for an opaque semiconductor with absorption coefficient α and $d \leq 1/\alpha$, is [27]

$$A_{\mathrm{LO}} = A_0[1 - \exp(-2\alpha d)]. \tag{4}$$

Here A_0 is the intensity observed in a low concentration or undoped crystal where the plasmon frequency is too low to affect the LO phonon [28]. Since the integrated Raman intensity is proportional to the scattering volume, it follows that

$$A_0 = \zeta_S A_{\mathrm{LOPC}} + A_{\mathrm{LO}}, \tag{5}$$

where $\zeta_S = I_{\mathrm{LO}}/I_{\mathrm{LOPC}}$ is the calculated area cross section from pure LO phonons and LOPC in a volume element, by Eq. 4. The depletion layer thickness for large hole concentrations can be estimated experimentally using equations Eqs. 4 and 5 by

$$d = \frac{1}{2\alpha} \ln \left(1 + \frac{\zeta_A}{\zeta_S} \right). \tag{6}$$

Here $\zeta_A = A_{\mathrm{LO}}/A_{\mathrm{LOPC}}$ is the ratio of the measured integrated intensities of the unscreened LO band from the depletion layer and the LOPC mode from the bulk. From the decomposition of the superimposed Raman features and equating Eqs. 3 and 6, we evaluate the hole concentration using

$$p = \frac{8\varepsilon_0 \varepsilon_S \alpha^2 \mathrm{V_B}}{e \left[\ln(1 + \frac{\zeta_A}{\zeta_S}) \right]^2}. \tag{7}$$

Figure 5(a) gives our experimentally derived values of ζ_A for $GaAs_{1-x}Bi_x$. Comparing I_{LO} for $x = 0$ with I_{LOPC} for $GaAs_{1-x}Bi_x$, leads to the ζ_S values in the inset. The intensity of the

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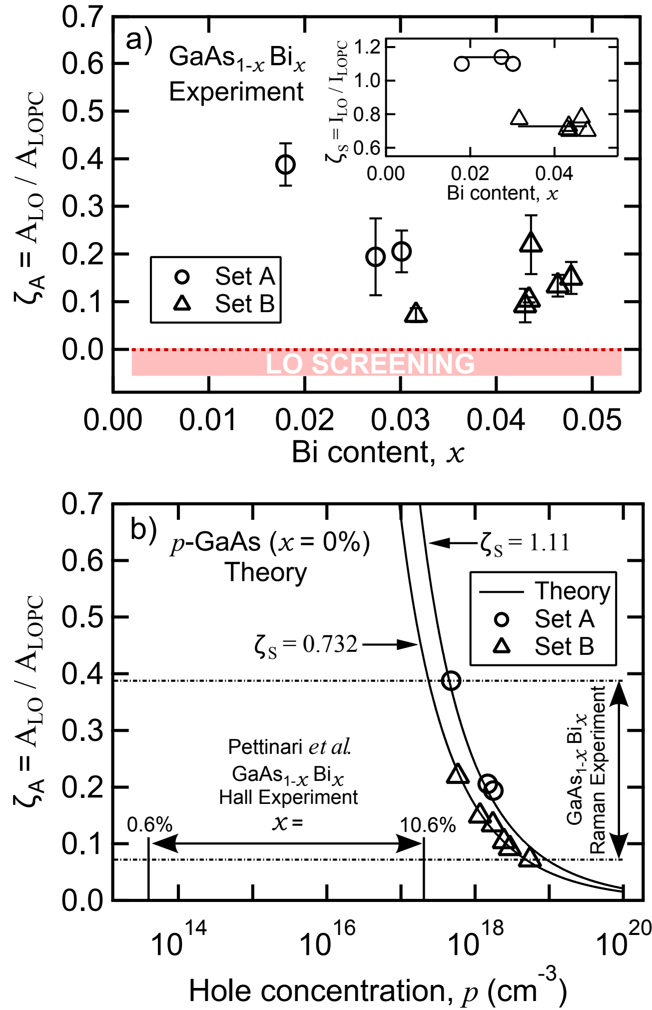

Fig. 5. (a) Experimentally determined values of ζ_A for all GaAsBi samples. (b) The theoretically expected [17] values of ζ_A (solid lines) for *p*-GaAs as a function of hole concentration. The horizontal and vertical ranges shown are from Pettinari *et al.* [12] and our optical measurements, respectively. The inset shows ζ_S for samples set A and B, used to calculate the two theoretical traces.

LOPC band increases relative to the unscreened LO mode for increasing x (see Fig. 3; the LO phonon contributions are greatly reduced for higher Bi contents). For the small Bi contents studied here, the LO band experiences almost total screening, due to the narrowing of the surface depletion layer. For comparison, the LO phonon in *p*-GaAs is only rendered invisible ($A_{LO}/A_{LOPC} \to 0$) for $p > 5\times10^{19}\,\mathrm{cm}^{-3}$, thus our observations here for *nominally undoped* GaAsBi are stunning.

Pettinari *et al.* [12] performed Hall-effect experiments on 30–56 nm thick $GaAs_{1-x}Bi_x$ epitaxial layers for $0.06 \le x \le 0.106$ and found that the hole concentration rose from $\sim 4\times10^{13}\,\mathrm{cm}^{-3}$ for $x = 0.6\%$ to $2.4\times10^{17}\mathrm{cm}^{-3}$ at $x = 10.6\%$. This suggests in our samples the carrier concentrations should not exceed $p \sim 3\times10^{15}\mathrm{cm}^{-3}$. To quantitatively evaluate p using Eq. 7, Bi-induced perturbations in the physical constants of the semiconductor must be con-

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sidered. Though the optical constants of GaAsBi are not well known, there are good estimates for changes in complex dielectric function and absorption coefficient [29, 30]; the band bending may be estimated assuming Fermi pinning at the Bi-induced acceptor states [11]. However, including these factors increases the spectroscopic estimation of p by only a factor of 2 to 4, rather than orders of magnitude. Alternatively, the hole concentration strongly depends on the values of ζ_A and ζ_S and the Raman efficiency of the LO phonon in theory can depend on x, which would abnegate use of a constant ζ_S. On close examination we find values for ζ_S differ between sets A and B, but are consistent across the same set. Thus it is reasonable to assume that ζ_S has weak Bi dependence over the range studied here and the difference between sets A and B is more likely due to their differing low optical qualities (caused by growing the epilayers away from stoichiometric conditions to introduce Bi into the GaAs matrix). Thus we present the theoretical [17] p dependence of ζ_A for the host p-type GaAs in Fig. 5(b). With a conservatively low [31, 32] value of $\zeta_S = 0.732$ we estimate the hole concentration to exceed $5 \times 10^{17}\text{cm}^{-3}$. The transport results of Pettinari *et al.* [12] are far smaller. Attempting to reconcile the two sets of results, we suggest our larger hole concentrations are due to thicker epitaxial layers. The thinner epilayers of Pettinari *et al.* [12] are closer to a pristine and evenly distributed GaAsBi system, with lower density of bismuth pair or cluster states than thicker layers [33]. On the other hand, we fully concur that hole concentrations rise with increasing Bi molar fraction. Theoretical examination into the formation of Bi-induced acceptor states located above the valence band during the growth may shed light on the discrepancy. The source of the single mode behavior in p-type GaAs has been traced to the intra-heavy-hole transitions, though for the simplified analysis presented here, contributions to the RS from intra-light-hole and inter-valence-band scattering mechanisms are omitted [15]. The GaAaBi band structure experiences most of its shift in the valence band and the acceptor state is pinned 26.8 meV above the valence band edge; these factors cannot be overlooked in better describing the strong damped hole-plasma-coupling phenomena.

4. Conclusion

To conclude, we have observed damped LOPC modes through Raman scattering experiments for *nominally undoped* $GaAs_{1-x}Bi_x$. By examining the redshifts and broadening of the GaAs-like LO, TO and LOPC bands, strong damping is found to dominate the phonon-hole-plasmon coupling, which softens well below ω_{TO} for large x. Our spectral analysis reveals that the native hole concentration correlates with the Bi molar fraction and exceed $5 \times 10^{17}\text{cm}^{-3}$. The comparatively large carrier densities measured here in a purely optical experiment are attributed to the relatively large thicknesses of our samples. Considering the extensively researched GaAs semiconductor, the results presented here represent an important contribution to further theoretical and experimental investigation of Bi incorporation in GaAs, as well as of the unusual properties of GaAsBi alloys.

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