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

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Abstract
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Keywords
undoped, gaasbi, optical, determination, carrier, concentration, nominally, coupling, plasmon, hole, phonon, raman, lo, scattering, reveals, strong

Disciplines
Engineering | Science and Technology Studies

Publication Details
Steele, J. A., Lewis, R. A., Henini, M., Lemine, O. M., Fan, D., Mazur, Y. I., Dorogan, V. G., Grant, P. C., Yu, S. & Salamo, G. J. (2014). Raman scattering reveals strong LO-phonon-hole-plasmon coupling in nominally undoped GaAsBi: optical determination of carrier concentration. Optics Express, 22 (10), 11680-11689.

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This journal article is available at Research Online: https://ro.uow.edu.au/eispapers/2255
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OCIS codes: (120.5820) Scattering measurements; (130.5990) Semiconductors; (140.3550) Lasers, Raman; (160.2100) Electro-optical materials; (170.5660) Raman spectroscopy.

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#205193 - $15.00 USD Received 27 Jan 2014; revised 29 Apr 2014; accepted 29 Apr 2014; published 7 May 2014 () 2014 OSA 19 May 2014 | Vol. 22, No. 10 | DOI:10.1364/OE.22.011680 | OPTICS EXPRESS 11680
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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 \( p = 2.4 \times 10^{17} \text{cm}^{-3} \) 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(\( \Gamma \)) 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 \( \omega_p \). 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 GaAs\(_{1-x}\)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 \( 10^{18} \text{cm}^{-3} \) [16].

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Fig. 1. Predicted [17] frequencies of the coupled modes (\( L_+ \) and \( L_- \)) and the plasma mode (\( \omega_p \)) as a function of hole concentration. The dashed line shows the general behavior of the single damped LOPC mode observed in \( p \)-GaAs.
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 $5 \times 10^{17} \text{cm}^{-3}$ and correlate with the Bi molar fraction. Interestingly, samples with larger Bi contents display significant or near total screening of the LO($\Gamma$) 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 $\mu$m and 0.3 $\mu$m, 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× 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 $-c(\vec{E}_{\text{incident}}, \vec{E}_{\text{scattered}})c$. For our samples, the epilayer thicknesses are large compared to the optical absorption depth $d_{\text{opt}} = 1/(2\alpha)$, 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 optical absorption depth $d_{\text{opt}} = 1/(2\alpha)$, 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.
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($\Gamma$) 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
dependence of the GaAs-like TO(Γ) and LO(Γ) modes in strained (100)-oriented GaAs$_{1-x}$Bi$_x$:

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

(1)

where the measured redshift value for the TO band is $\Delta \omega_{\text{TO}} = -27(\pm 4)\:\text{cm}^{-1}$ and the value for the LO phonon redshift agrees well with our previous study [18] at $\Delta \omega_{\text{LO}} = -71(\pm 3)\:\text{cm}^{-1}$. Figure 1 indicates that for low hole doping the LOPC mode is slightly blueshifted relative to $\omega_{\text{LO}}$ before redshifting towards $\omega_{\text{TO}}$ (crossing at $p \sim 5 \times 10^{18} \:\text{cm}^{-3}$) with increasing hole concentrations and reaching $\omega_{\text{TO}}$ at higher concentrations ($p \geq 5 \times 10^{20} \:\text{cm}^{-3}$). 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 $10^{18} - 10^{20} \:\text{cm}^{-3}$ 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 $\omega_{\text{TO}}$ than $\omega_{\text{LO}}$. 

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.
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, $\Omega_{\text{GaAs}}^2 = (\omega_{\text{LO}}^2 - \omega_{\text{TO}}^2)$ [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-plasmon interaction in GaAsBi. The damping constant of the plasma oscillation $\Gamma_p$ can be evaluated by the hole scattering rate as

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

(2)

where $e$ is the electrical charge, $\tau$, $\mu$, and $m^*$ are the average scattering relaxation time, hole mobility, and effective mass of the free carrier, respectively. The intrinsically low hole mobility $\mu_h$, 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 $\mu_h$ for GaAs$_{1-x}$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 $\omega_p$ crossing $\omega_{\text{LO}}$. 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
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

\[
d = \left( \frac{2\varepsilon_0\varepsilon_S V_B}{e\rho} \right)^{1/2},
\]

where \(V_B \) and \(\varepsilon_S\) are the band bending and static dielectric constant, respectively. The inverse relationship of \(d\) on \(\rho\) 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 \(\alpha\) and \(d \leq 1/\alpha\), is \[27\]

\[
A_{LO} = A_0 \left[1 - \exp(-2\alpha d)\right].
\]

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

\[
A_0 = \zeta_S A_{LOPC} + A_{LO},
\]

where \(\zeta_S = I_{LO}/I_{LOPC}\) 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

\[
d = \frac{1}{2\alpha} \ln \left(1 + \frac{\zeta_A}{\zeta_S}\right).
\]

Here \(\zeta_A = A_{LO}/A_{LOPC}\) 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

\[
p = \frac{8e_0\varepsilon_S\alpha^2 V_B}{e \left\{ \ln(1 + \frac{\zeta_A}{\zeta_S}) \right\}^2}.
\]

Figure 5(a) gives our experimentally derived values of \(\zeta_A\) for GaAs\(_{1-x}\)Bi\(_x\). Comparing \(I_{LO}\) for \(x = 0\) with \(I_{LOPC}\) for GaAs\(_{1-x}\)Bi\(_x\), leads to the \(\zeta_S\) values in the inset. The intensity of the
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 ($\zeta_{LO}/\zeta_{LOPC} \to 0$) for $p > 5 \times 10^{19}$ 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 $\leq x \leq 0.106$ and found that the hole concentration rose from $\sim 4 \times 10^{13}$ cm$^{-3}$ for $x = 0.6\%$ to $2.4 \times 10^{17}$ cm$^{-3}$ at $x = 10.6\%$. This suggests in our samples the carrier concentrations should not exceed $p \sim 3 \times 10^{15}$ cm$^{-3}$. To quantitatively evaluate $p$ using Eq. 7, Bi-induced perturbations in the physical constants of the semiconductor must be con-
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 $\zeta_A$ and $\zeta_S$ and the Raman efficiency of the LO phonon in theory can depend on $x$, which would abnegate use of a constant $\zeta_S$. On close examination we find values for $\zeta_S$ differ between sets A and B, but are consistent across the same set. Thus it is reasonable to assume that $\zeta_A$ 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). Therefore, we present the theoretical [17] $p$ dependence of $\zeta_A$ 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 $5 \times 10^{17}$ 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 GaAs:Bi 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 GaAs:Bi 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 $\omega_{TO}$ for large $x$. Our spectral analysis reveals that the native hole concentration correlates with the Bi molar fraction and exceeds $5 \times 10^{17}$ 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 GaAs:Bi alloys.

Acknowledgments

We thank the Australian Research Council for support and acknowledge the contributions of S. Novikov. O. M. Lemine and M. Henini acknowledge King Abdul-Aziz City for Sciences and Technology (KACST) for financial support. The work in University of Arkansas was supported by NSF Career Award No. DMR-1149605.