

Raman studies on $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$

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The lattice vibrational properties of new semiconductor alloys, $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$, are reported. These alloys, which were grown by metalorganic vapor phase epitaxy technique, contain a small amount (1.2%–3.8%) of Bi. A detail Raman scattering study of these new alloys, which exhibit weak temperature dependence of the band gap with increasing amount of Bi, is reported here. Good crystalline quality and spatial homogeneity was confirmed using micro-Raman technique. The alloys show ternary compound behavior, confirming substitutional incorporation of Bi into the lattice site. New vibrational modes observed were assigned to GaBi-like and InBi-like modes. In addition, phonon-plasmon coupled modes and vibrational modes corresponding to Bi and As materials were also observed. Results are discussed to characterize these new alloys in detail.

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I. INTRODUCTION

The temperature-insensitive semiconductor laser is one of the future key devices in the field of optical communications. Oe and Asai^{1,2} have recently proposed a new III–V semiconductor alloy containing semiconductor and semi-metal components. These alloys are expected to show weak temperature dependence of the band gap, and therefore are strongly promising candidates for the development of a new series of semiconductor lasers whose emission wavelength stays nearly constant through the ambient temperature variation. Initial studies^{1–5} indicate that a bismuth-containing III–V compound material, particularly GaInAsBi, is suitable for such lasers. In this material, a small amount of Bi is incorporated into the As site. In order to understand the optoelectronic properties of GaInAsBi compound, it is important first to study the constituent alloys $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ for their optical, vibrational, and electronic properties. An in-depth study of the fundamental physical properties of these promising materials is strongly needed in order to explore their potential for commercial usage. In the recent past,^{1–4} both constituent alloys $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ were successfully grown by the metalorganic vapor phase epitaxy (MOVPE) technique for Bi content ranging from $x=1.2\%$ to 3.8% and it was confirmed that the temperature dependence of the alloy-band gap decreases with increasing Bi content. The band gaps of these samples were estimated using photoluminescence (PL)³ and optical transmission measurements.⁵ The PL peak position and the absorption-edge were found to shift towards low energy with

increasing Bi content in the sample. A temperature-dependent study confirms that, with increasing amount of Bi, the alloy-band gap versus temperature curve tends to become flat and the temperature dependence of the alloy-band gap ($\Delta E_g/\Delta T$) decreases. The crystalline quality and the Bi content of these samples were investigated using regular characterization techniques.^{1–6} The crystal surface quality was examined by taking surface images using the Nomarski-interference-contrast microscope and scanning electron microscope (SEM). After optimizing the growth conditions, mirror-like surfaces were obtained for all samples. The Bi content in these alloy samples was estimated using SIMS and Rutherford backscattering (RBS) analysis. It was observed that more than 90% of Bi was substitutionally incorporated into the host GaAs and InAs zinc-blende lattices. Crystalline qualities of the epilayers were investigated using x-ray diffraction measurements.^{3,4} It was observed that the diffraction peak shifts towards larger lattice constant with increasing amount of Bi content. Clearly distinguishable narrow $K\alpha_1$ and $K\alpha_2$ peaks related to $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ lattices were observed, which confirm good crystal quality, in spite of the fact that the samples were grown at low temperatures.

This article presents a study of the vibrational properties of the constituent alloys $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ using Raman scattering. Raman spectroscopy is a powerful nondestructive technique to study the fundamental properties of compound materials. On one hand, Raman scattering can be used to study the crystalline quality including residual stress and compositional fraction x , and on the other hand one can study the electronic and vibronic properties of the material including charge carrier activation and mobility. Some initial

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results of Raman scattering studies on these materials were recently reported.⁷⁻⁹ In this article, we report a detailed Raman scattering study on MOVPE grown epilayers of $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ alloys. Good single crystalline growth with spatial homogeneity was confirmed for all samples using the micro-Raman technique. The two-mode behavior of Raman spectra observed for these samples indicates ternary alloy nature for both $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ materials, confirming incorporation of Bi into the lattice site. New vibrational modes were observed in Raman spectra of these compounds, which are assigned to GaBi- and InBi-like vibrational modes for the two compounds, respectively. Since the Bi content is much lower than the As content in these samples, the GaBi- and InBi-like vibrational modes are much weaker compared to the GaAs- and InAs-like vibrational modes. In addition, Raman spectra also show As-related vibrational modes, disorder-activated modes, and phonon-plasmon coupled modes arising from the interaction of the free charge carriers with the crystalline vibrational modes. Vibrational modes of Bi material were also observed. Experimental results confirm that Bi atoms are substitutionally incorporated into the As-site and the resultant crystals have good crystalline structures of $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ ternary compounds. The experimental observations are discussed in detail.

II. EXPERIMENT

A. Sample details

The samples studied here are 0.5 μm thick $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ epilayers grown in a horizontal low-pressure (about 60 Torr) MOVPE system. The $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ epilayers were grown on (100) oriented Si-doped GaAs and InAs substrates, respectively. The Bi content, x , varies from 1.2% to 2.4% (0.012–0.024) in $\text{GaAs}_{1-x}\text{Bi}_x$ samples and from 1.6% to 3.8% (0.016–0.038) in $\text{InAs}_{1-x}\text{Bi}_x$ samples. These compositions were calculated from the lattice constants of the alloys, which were determined using x-ray diffraction studies, taking account of the lattice deformations. These alloys seem to have a large miscibility gap, therefore a fairly low growth temperature is required to grow a metastable alloy. It was possible to grow these samples at a temperature as low as 365 °C with a reasonable growth rate of about 1 $\mu\text{m}/\text{h}$. The epilayers were cut into a size of a square of cm for Raman scattering measurements. More details of the growth process can be found elsewhere.^{3,4}

B. Raman setup

Room-temperature Raman scattering experiments were performed in backscattering geometry using the 514.5 nm line of an Ar-ion laser, Spex double monochromator, CCD detector, and the usual optics and electronics. In order to avoid local heating and formation of laser-activated plasma in the samples, low laser power was used. Excitation power density was further reduced by using a cylindrical focusing lens. The spectrometer was properly aligned and calibrated to achieve a spectral accuracy of about 0.2 cm^{-1} . Using a high precision microscope, it was possible to have a spatial

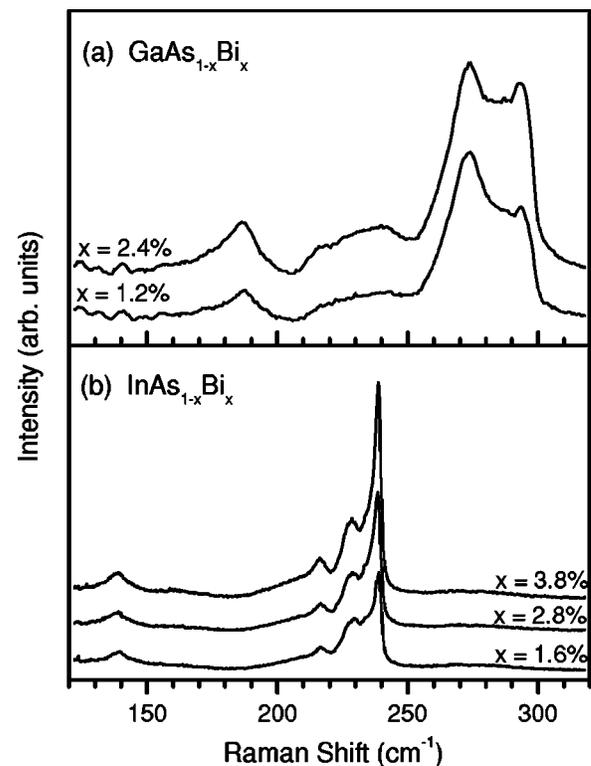


FIG. 1. Room-temperature Raman spectra from (a) $\text{GaAs}_{1-x}\text{Bi}_x$ and (b) $\text{InAs}_{1-x}\text{Bi}_x$ epilayers. Bi content of each sample is indicated in the figure.

resolution of about a micron, which was necessary to investigate the spatial homogeneity of the samples.

III. RESULTS AND DISCUSSION

Room-temperature Raman spectra were measured from various $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ epilayers. In order to investigate the spatial homogeneity of the physical properties of these crystals, the samples were scanned by micro-Raman technique and the spectra were measured from various points throughout the sample surface. For each sample, Raman spectra measured from various points on the surface show no difference in phonon frequencies or line shapes, confirming good spatial homogeneity of crystal properties. Figures 1(a) and 1(b) present one of such a spectrum from each $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ samples, respectively. The Bi content, x , for each sample is indicated in the figure. Raman spectra from the $\text{GaAs}_{1-x}\text{Bi}_x$ samples in Fig. 1(a) show three prominent structures at about 190, 268, and 290 cm^{-1} and two broad structures between 210 and 250 cm^{-1} and between the prominent structures at 268 and 290 cm^{-1} . A weak structure can also be seen at about 140 cm^{-1} . Similarly, Raman spectra from the $\text{InAs}_{1-x}\text{Bi}_x$ samples in Fig. 1(b) contain a prominent structure at 239 cm^{-1} , a structure at 216 cm^{-1} , and weak broad structures near 140 and 230 cm^{-1} . A weak structure near 160 cm^{-1} and a tail between 200 and 216 cm^{-1} can also be seen.

To the best of our knowledge, apart from some of our preliminary reports,⁷⁻⁹ there is as yet no Raman scattering study on these alloys. Therefore, in order to understand the vibrational spectra of these alloys, we have to compare them

with the vibrational spectra of the parent host lattices, GaAs and InAs, and with the vibrational spectra of standard III–V ternary compounds, like $\text{GaAs}_{1-x}\text{P}_x$ and $\text{InAs}_{1-x}\text{P}_x$. These samples also contain some impurity atoms which are incorporated into the crystal during the growth process. Carbon is one of the main incorporates, which is a well known acceptor in GaAs and InAs materials. Therefore, Raman spectra from these samples should also be compared with those from standard *p*-type III–V materials.

Typical first-order backscattered Raman spectra from the (100) surface of GaAs and InAs contain LO phonons at 291 and 241 cm^{-1} , respectively. In the case of slight deviation from (100) orientation, or from true backscattering geometry, the forbidden TO phonons can also be observed at 268 and 220 cm^{-1} , respectively. Looking at a standard Raman spectrum of the ternary compound $\text{GaAs}_{1-x}\text{P}_x$ ($\text{InAs}_{1-x}\text{P}_x$), one finds that this compound shows a “two-mode” behavior with simultaneous presence of both GaAs(InAs)- and GaP(InP)-like phonon modes. The strengths and the frequency positions of these phonons depend on the amounts of the constituent contents. If we treat our samples as ternary compounds, we expect to observe both GaAs(InAs)-like and GaBi(InBi)-like phonon modes in Raman spectra. However, one must remember that in these samples the Bi content is very low compared to the As content. Normally, a typical ternary compound contains comparable amounts of each constituents. Therefore, the GaBi(InBi)-like mode is expected to be much weaker compared to the GaAs(InAs)-like mode. Furthermore, free charge carriers in a semiconductor couple strongly with the lattice vibrations, and Raman spectra from such a material contain so called phonon-plasmon coupled modes, which normally appear in doublet (L^- and L^+ modes). However, it has been shown by various researchers^{10–14} that in a *p*-type III–V material only one coupled mode is observed, which changes its frequency position from near-TO-phonon-frequency to near-LO-phonon-frequency, in dependence of the carrier concentration.

Coming back to Fig. 1, one finds that Raman spectra from $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ samples do contain GaAs- and InAs-like phonons, respectively. The structures at 216 and 239 cm^{-1} in Fig. 1(b) are the InAs-like TO and LO phonons, respectively. Similarly, the structure 290 cm^{-1} observed in Fig. 1(a) is the GaAs-like LO phonon. The other prominent structure near 268 cm^{-1} in $\text{GaAs}_{1-x}\text{Bi}_x$ samples has a contribution from GaAs-like TO phonon, as well as from phonon-plasmon coupled mode, which will be discussed later. Apart from these optical phonons, several additional structures can be seen in Fig. 1, which are discussed in the following.

A. Bi-related vibrational modes

Since solubility of Bi is very small (about 0.025%) in both GaAs and InAs materials, hence it is expected that Raman spectra from our samples may contain some Bi-related vibrational modes, which arise from the vibrations of undissolved Bi. In order to investigate this, we measured Raman spectra from pure Bi and Bi_2O_3 materials, and compared them with Raman spectra from our samples. No vibrational structure present in the Raman spectrum of Bi_2O_3 was ob-

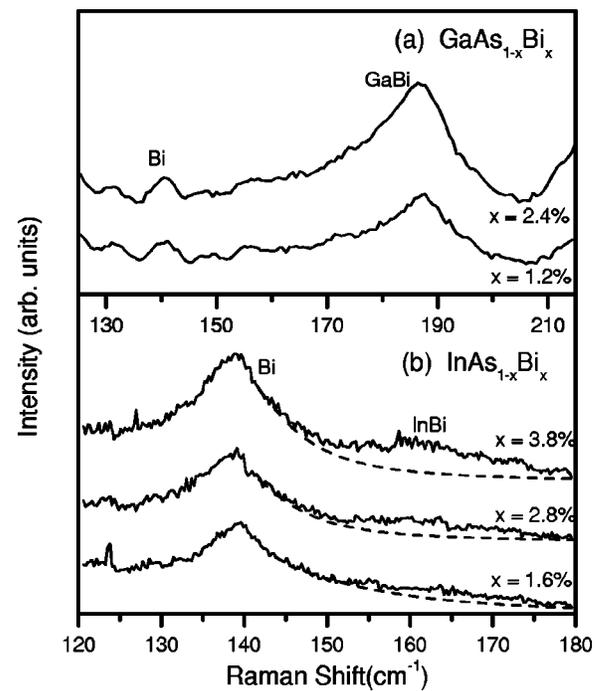


FIG. 2. New structures assigned to GaBi-like and InBi-like vibrational modes observed in Raman spectra from (a) $\text{GaAs}_{1-x}\text{Bi}_x$ and (b) $\text{InAs}_{1-x}\text{Bi}_x$ epilayers. In addition, all samples contain a Bi-related structure near 140 cm^{-1} .

served in Raman spectra of our samples. This rules out any possibility of oxide formation on the surface. Raman spectrum of Bi material contains a prominent structure near 141 cm^{-1} . A weak structure can be observed at about 140 cm^{-1} for all $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ samples. A closer look at the Bi-related modes in both $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ samples is shown in Fig. 2. One may recall that the 2TA phonon mode for GaAs appears at the same frequency position. It was confirmed by comparing with Raman spectra of InAs that this structure does not have any contribution from the InAs lattice but, since this structure is observed in $\text{InAs}_{1-x}\text{Bi}_x$ samples as well, and in fact, it is much more prominent for the $\text{InAs}_{1-x}\text{Bi}_x$ samples than for the $\text{GaAs}_{1-x}\text{Bi}_x$ samples, we assign this structure to Bi-related vibrational mode. The reason, that this structure is weaker for $\text{GaAs}_{1-x}\text{Bi}_x$ samples compared to for $\text{InAs}_{1-x}\text{Bi}_x$ sample, could be that the solubility of Bi is better in GaAs than in InAs. As expected, the intensity of this structure also shows a weak dependence on the Bi content of samples.

B. GaBi- and InBi-like vibrational modes

Since it was confirmed from x-ray and RBS measurements that Bi atoms are substitutionally incorporated into the lattice for both $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ samples, we expect Raman spectra from these samples to exhibit a two-mode behavior, like many other III–V ternary compounds. Therefore, we expect to observe GaBi- and InBi-like vibrational modes in Raman spectra of these samples. Such vibrational modes have not been reported, and hence the frequency positions of such vibrational modes are not known. In order to identify such vibrational modes in Raman spectra

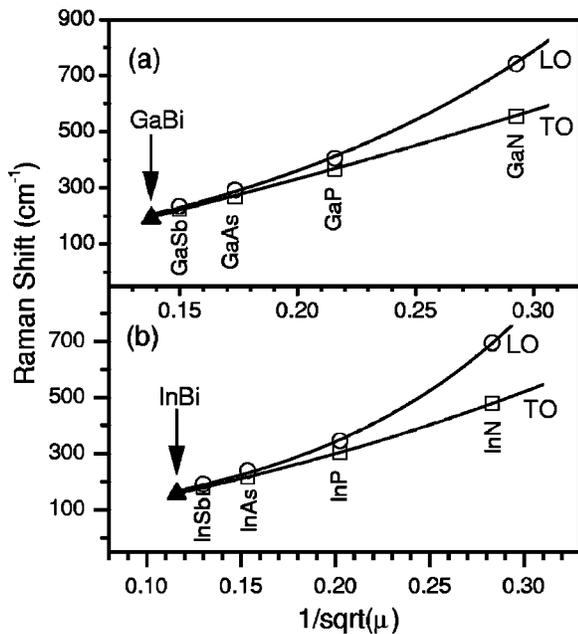


FIG. 3. The circles and the squares represent LO and TO phonon frequencies, respectively, for (a) GaX and (b) InX materials in dependence of $1/\sqrt{\mu}$, where $X=N, P, As,$ and Sb . The TO and the LO phonon frequencies for GaBi and InBi materials can be obtained from extrapolations of the fits.

of our samples, we theoretically estimated the frequency positions of GaBi and InBi vibrational modes. For this, we used a simple model based on harmonic GaX and InX oscillators, with $X=N, P, As,$ and Sb , the elements from group V in the periodic table. The Raman frequencies of the optical phonons for GaX and InX are well known in the literature, which are plotted in Fig. 3 (shown by the open circles and squares) in dependence of $1/\sqrt{\mu}$, where μ is the reduced mass of X. The curves in Fig. 3 are simple fits to the TO and LO phonon frequencies, extrapolations of which give TO and LO phonon frequencies for $X=Bi$, the next element of group V in the sequence N–Sb. The estimated values of LO and TO phonon frequencies are 196 and 189 cm⁻¹, respectively, for GaBi, and 161 and 155 cm⁻¹, respectively, for InBi materials. As shown in Fig. 2, we have observed a structure at about 189 cm⁻¹ for GaAs_{1-x}Bi_x samples and a weak structure at about 160 cm⁻¹ for InAs_{1-x}Bi_x samples, which we assign to the GaBi-like and InBi-like vibrational modes, respectively. Since these modes are weak and broad, we do not expect to observe GaBi-like and InBi-like TO and LO phonons independently. As discussed before, the weak Raman scattering intensities of these modes compared to those of GaAs-like or InAs-like modes are understandable, because the Bi contents in these samples are much smaller than the As contents. Furthermore, it can be noted that the InBi-like modes in Fig. 2(b) are weaker compared to the GaBi-like modes in Fig. 2(a). This further suggests that the solubility of Bi is better in GaAs compared to InAs. As one may expect, both GaBi and InBi vibrational modes increase with increasing Bi content.

C. As-related and disorder-activated modes

Apart from the above discussed structure, one broad structure between 210 and 250 cm⁻¹ can be seen in Fig. 1(a)

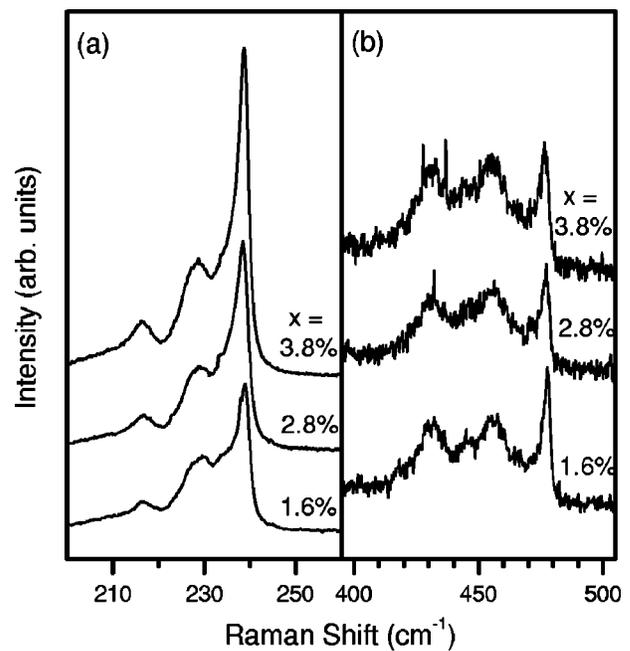


FIG. 4. Raman spectra from InAs_{1-x}Bi_x epilayers in the spectral range of (a) first- (b) second-order optical phonons.

for the GaAs_{1-x}Bi_x samples. This structure is similar to previously observed¹⁵ vibrational modes corresponding to As clusters in GaAs. When Bi atoms are incorporated into the lattice site, because of the low growth temperature, the knocked-out As atoms may form such clusters in the samples, which shows up in Raman spectra. A similar structure between 220 and 240 cm⁻¹ can also be observed in Raman spectra from the InAs_{1-x}Bi_x samples, however this structure is overlapped with InAs-like optical phonons. It was confirmed by comparing it with the Raman spectrum of Bi material that this structure does not have any Bi-related origin. However, with increasing incorporation of Bi, the amount of knocked-out As atoms also increases, and hence the strength of this structure has a weak dependence on the Bi content of the samples. Furthermore, the InAs-like optical phonons in InAs_{1-x}Bi_x samples contain a tail-like shoulder structure in the low-frequency side. A similar tail is also present for the GaAs_{1-x}Bi_x samples, but it overlaps with other structures. The origin of this structure is not very clear, but it could be related to the relaxation of the momentum selection rules due to incorporation of Bi atoms. This structure was absent in the epilayers grown without Bi, however, it has no relation with Bi-related vibrations, because no such structure was observed in Raman spectrum of Bi material. Such modes, which correspond to the combined density-of-states, have been observed in Raman spectra of ternary alloys. They are often called disorder-activated modes.

Figure 4 shows a comparison of the first- and the second-order InAs-like optical phonons with respect to the Bi content for the InAs_{1-x}Bi_x samples. The intensity of the first-order phonon increases with increasing Bi content, whereas the intensities of second-order phonons show a slight decrease with increasing Bi content. Similar results are also observed for the GaAs_{1-x}Bi_x samples, however, the in-

crease of intensity for the first-order phonon for these samples is comparatively weak. This behavior can be explained by invoking the resonance effect. The fundamental gaps (E_0) for both InAs and GaAs at room temperature are much below the excitation laser energy, 2.41 eV. However, the E_1 gaps at the saddle point are 2.50 eV for InAs and 2.89 eV for GaAs,¹⁶ both slightly above the excitation energy. Resonance effects at the E_1 gap for III–V binary and ternary compounds have been well studied^{17–19} in the past. In our case, the alloy-band-gap decreases with increasing Bi content.^{3,5} Therefore, the first-order phonon exhibits a resonance enhancement with increasing amount of the Bi content. Since the E_1 gap of InAs, compared to that of GaAs, is closer to the excitation energy, InAs_{1–x}Bi_x samples show stronger resonance effect. Resonance enhancements in first-order phonons are stronger than those in the second-order phonons.¹⁸ Second-order phonons in our samples do not show any resonance enhancement with increasing Bi content when excited at 2.41 eV. The decreasing intensities of second-order phonons in our samples can be explained by relaxation in the momentum selection rules with increasing Bi content. Second-order phonon modes are more sensitive to the relaxation in the selection rules, and hence their intensities decrease with increasing amount of Bi. This further supports our earlier explanation about relaxation in the selection rules. However, the Bi content is still too small to affect the strength of the first-order phonons, where the resonance enhancement remains dominant.

D. Phonon-plasmon coupled mode

Furthermore, Raman spectra for the GaAs_{1–x}Bi_x samples show a prominent structure near GaAs-like TO phonon, and some structures between InAs-like TO and LO phonons for the InAs_{1–x}Bi_x samples, as seen in Fig. 1. Such structures are signatures of the presence of charge carriers in the samples. In polar semiconductors, the LO phonon couples strongly with collective oscillations of the free-carriers (plasma) due to the macroscopic electric fields associated to both kinds of elementary excitations. Raman scattering is an extremely useful tool to obtain information about such LO-phonon-plasmon coupled (LOPC) modes. Because of the two-mode behavior of many ternary III–V alloys, the features of the coupled modes for these alloys are slightly different from those for binary materials, as have been reported for AlGaAs^{20,21} or InGaAs.^{10,22} Furthermore, the behaviors of the coupled modes are different for the *n*- and *p*-type materials. It has been demonstrated through extensive studies^{11,12,23} on GaAs that the plasmon damping has a profound effect on the phonon-plasmon coupling for *p*-type materials, because of large hole effective mass and lower mobility. Unlike in *n*-type materials, the large plasma damping in *p*-type materials makes Raman spectra exhibit only one LOPC mode, whose frequency remains in the vicinity of the optical phonons. In contrast to the *n*-type materials, carrier-concentration dependence of the LOPC mode is weak in *p*-type materials.^{10,12,23} This implies that the plasmon damping effect plays a dominant role in the phonon-plasmon coupling. The coupling between lattice vibrations and plasma in

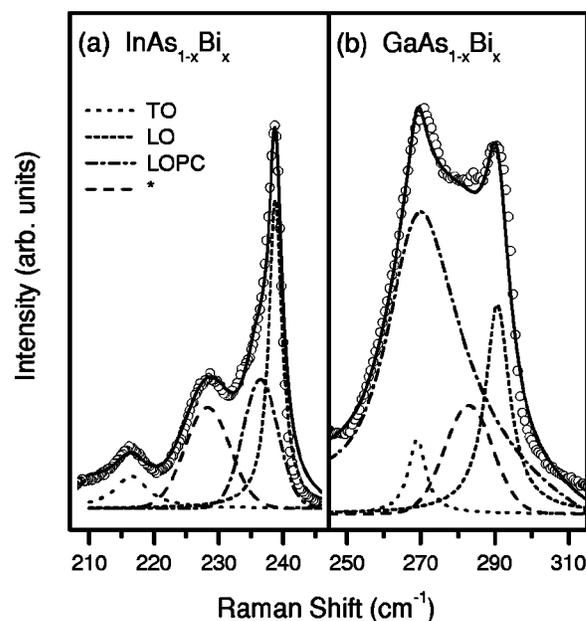


FIG. 5. Deconvolution of the first-order Raman spectra from (a) InAs_{1–x}Bi_x and (b) GaAs_{1–x}Bi_x epilayers. Experimental data are presented by circles and best fits by full lines. Apart from the listed contributions, the structure indicated by asterisk at 228 cm^{–1} in (a) is related to As vibrational modes. The origin of a similar mode at 283 cm^{–1} in (b) is still not clear.

these materials takes place through the interaction between the LO phonon and a strongly damped plasmon mode. The large damping shifts the frequency and broadens the line-width of the LOPC mode.^{12,23} This damping is more pronounced in the case of ternary epilayers compared to binary bulk materials, because ternary epilayers have additional carrier scattering mechanism, such as alloy scattering or dislocation induced by lattice mismatch between the epilayer and substrate.

Figure 5 shows a closer look at the InAs- and GaAs-like first-order optical phonon spectral range for the InAs_{1–x}Bi_x and the GaAs_{1–x}Bi_x samples with maximum Bi content. As shown in Fig. 5, apart from two Lorentzians corresponding to the TO and the LO phonons, best fits to the experimental spectra requires two more structures. One of these two structures is the LOPC mode and the other appears to be the As-related mode for the InAs_{1–x}Bi_x samples and a disorder activated mode for the GaAs_{1–x}Bi_x samples. The intensities of these modes have some dependence on the Bi content of the samples, however, we do not find any direct relation of these modes with Bi. The elements Bi and As are from the same group of the periodic table, therefore, an incorporation of Bi does not give rise to any carrier activation. However, carbon contamination is well-known for MOVPE growths carried out at low temperatures. Carbon is a known acceptor for many III–V semiconductors. Since the samples discussed here were grown at a temperature as low as 365 °C, it is expected that these samples contain carbon contamination. Standard characterization results from SIMS indicate that all the samples studied here contain carbon impurity. The InAs_{1–x}Bi_x samples contain low carbon contamination, but carbon concentration in GaAs_{1–x}Bi_x samples is over 10¹⁸ cm^{–3}. As discussed by Wan and Young²³ for *p*-type GaAs, a

single LOPC mode observed has a weak dependence on the carrier concentration. With increasing amount of carrier concentration, this LOPC mode first appears near the LO-phonon frequency with weak intensity, and then shifts towards the TO-phonon frequency with increased intensity. As seen in Fig. 5(a), the deconvolution of Raman spectrum for the $\text{InAs}_{1-x}\text{Bi}_x$ sample contains four structures at 216, 228, 237, and 239 cm^{-1} . The structure at 216 cm^{-1} is the InAs-like TO phonon. This phonon is forbidden for backscattering from the (100) surface. Appearance of a weak TO phonon is due to a slight deviation from (100) surface orientation, from true backscattering geometry, and due to relaxation of the momentum selection rules. The structure at 239 cm^{-1} is the uncoupled InAs-like LO phonon, which comes from the depletion layer. In the frequency range between the TO and LO phonons, the real part of the dielectric function is negative for pure lattice vibrations, therefore, an electromagnetic wave associated to the lattice vibrations cannot propagate in this region. The broad structure near 228 cm^{-1} between the TO and LO phonons appears to be due to As-related vibrations, which are also observed for the $\text{GaAs}_{1-x}\text{Bi}_x$ samples in the same frequency range. The origin of this structure is discussed. We attribute the other structure at 237 cm^{-1} to the LOPC mode. Since $\text{InAs}_{1-x}\text{Bi}_x$ samples contain a small amount of charge carriers, this LOPC mode appears very close to the LO phonon and has weak intensity.

Similarly, the deconvolution of Raman spectrum from the $\text{GaAs}_{1-x}\text{Bi}_x$ sample in Fig. 5(b) contains four structures at 268, 270, 283, and 290 cm^{-1} . The structures at 268 and 290 cm^{-1} are GaAs-like TO and the uncoupled LO phonons, respectively. Appearance of the symmetry-forbidden TO phonon has the same reason as previously discussed for the $\text{InAs}_{1-x}\text{Bi}_x$ sample. The broad structure at 270 cm^{-1} is attributed to the LOPC mode. The $\text{GaAs}_{1-x}\text{Bi}_x$ samples have a large amount of carriers, therefore, the uncoupled LO phonon mode is weak and the LOPC mode appears near the TO phonon frequency with strong intensity. Large linewidth of the LOPC mode indicates heavy damping of plasmon in these samples. The line shapes of the LOPC modes for each sample were calculated following the process discussed in Ref. 23. For all $\text{GaAs}_{1-x}\text{Bi}_x$ samples, we need one additional structure near 283 cm^{-1} to fit the experimental spectra. The origin of this structure is not very clear at present. Since these samples contain a large amount of carbon, one may consider the possibility of carbon-related vibrational modes. However, carbon local vibrational modes (CLVM) normally appear at higher frequencies (above 500 cm^{-1}), therefore, this structure does not appear to be the CLVM. A similar structure between the TO and the LO phonons was observed in the past²⁴ for GaAsP crystals, where the authors attributed this mode to the oscillation of phosphorus at the edge of the Brillouin zone, made Raman active by disorder. A similar possibility exists for oscillation of carbon in our samples, however, it has not been confirmed. The other possibility is that this structure could be a disorder activated or a Fröhlich mode. Such modes have also been observed between the TO and the LO phonons in the past^{25,26} for ternary alloys. In fact, since this structure is deeply buried into the LOPC mode, an unambiguous deconvolution of this structure is difficult. The

line shape of this structure depends on the free parameters used to fit the line shape of the LOPC mode. We conclude this part by noting that more experiments are needed to elucidate the origin of this structure. A more detailed investigation of the LOPC mode and a numerical estimation of the charge carrier concentration as well as the hole mobility will help in understanding the character of this mode.

IV. CONCLUSIONS

Room-temperature Raman spectroscopic studies on epilayers of $\text{GaAs}_{1-x}\text{Bi}_x$ and $\text{InAs}_{1-x}\text{Bi}_x$ with Bi content ranging from 1.2% to 3.8%, are reported. These new materials, which tend to have temperature-insensitive band gap with increasing amount of Bi, were grown at low temperature using the low-pressure MOVPE technique. Micro-Raman spectra measured from various points on each sample indicate good crystalline quality with spatial homogeneity. It was observed through Raman scattering that all the samples show ternary-alloy behavior where Bi is substitutionally incorporated into the lattice site replacing some of the As atoms. New structures observed in Raman spectra are assigned to GaBi- and InBi-like vibrational modes. These new modes show a weak dependence on the Bi content of the samples. In addition, Bi- and As-related vibrational modes were observed. Bi-related modes indicate that the solubility of Bi is better in GaAs than in InAs. Furthermore, Raman spectra from these samples show phonon-plasmon coupled modes, which arise from the coupling between the LO phonon and the free charge carriers in the samples. Carbon, which is incorporated into the lattice as contamination during the growth process, is an acceptor in these samples. The $\text{GaAs}_{1-x}\text{Bi}_x$ samples have a larger amount of carbon contamination compared to the $\text{InAs}_{1-x}\text{Bi}_x$ samples, which is also shown up in Raman spectra. A detailed Raman investigation of these new semiconductor-semimetal alloys have been reported here for the first time.

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