Resonant Raman scattering probe of alloying effect in $GaAs_{1-x}P_x$ ternary alloy semiconductors

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A comparative study of the alloying effect in $GaAs_{1-x}P_x$ ($x=0.90,\ 0.65$) ternary alloy semiconductors, using resonant Raman spectroscopy as a probe, is presented. Energy-shifted first-order Raman modes between 600 and 800 cm^{-1} and between 1100 and 1200 cm^{-1} near resonance is observed. Anomalous enhancement in the oscillator strength for the second-order resonance is observed. These effects can only be understood if the relevant resonant intermediate state is a localized sharp exciton interacting strongly with the LO phonon forming a localized exciton-phonon complex. First-order resonance is found to have contributions from direct band transition and localized excitons, whereas for the second-order and third-order resonances, contribution is only from localized excitons. Increase in localization, binding energy, and lifetime of the excitons is observed with increasing disorder. [S0163-1829(96)09531-8]

I. INTRODUCTION

Study of III-V alloy semiconductors has become a subject of considerable interest because of their wide range of applications in different fields of science and technology. The alloying extends the flexibility of tailoring the optoelectronic properties in the spectral region intermediate to constituent binary semiconductors.[1] The III-V ternary alloy semiconductors of the form $(A_xB_{1-x})C$, where A and B are either anions or cations, are formed when a group-III or a group-V atom is substituted by another atom of the same group. These alloys exhibit lattice periodicity, and long-range order with the difference that atoms A and B are distributed randomly at the center of the face-centered-cubic lattice, with a concentration-dependent mean density, and the center of the cubic lattice is occupied to atom C. In these ternary semiconductor alloys, atoms of the constituent binary semiconductors are randomly oriented, leading to fluctuations in masses and force constants in the neighborhood referred as compositional disorder.

Compositional disorder introduces changes in the electronic properties of alloy semiconductors. The effect of disorder is either to smear out the band edge or to introduce localized states in the forbidden gap. In the former case, resonance features will be broadened and in the latter case, a sharp resonance feature is observed. Balkanski *et al.*[2] and Jain, Soni, and Abbi[3] have investigated the effect of disorder on the electronic properties of $Ga_{1-x}In_xP$ and $GaAs_{1-x}P_x$ and found a replica of the first-order Raman mode energy shifted to the high-frequency region near resonance. Also, the Raman spectrum of ternary alloy semiconductors is qualitatively different from binary semiconductors at resonance. For GaP,[4] all allowed phonons exhibit resonance enhancement and the structure of the two-phonon spectrum remains intact, whereas in $GaAs_{1-x}P_x$ mixed crystal, the two-phonon spectrum disappears and instead an energy shifted one-phonon spectrum appears. These authors[2,3] have also observed anomalous enhancement in the intensity of the GaP-like 2LO(Γ)-phonon mode compared to the 1LO (Γ)-phonon mode in $GaAs_{1-x}P_x$. Furthermore, the oscillator strength for the 2LO(Γ)-phonon mode is comparable to that of the 1LO(Γ)-phonon mode. For GaP, on the other hand, the intensity of the 2LO-phonon mode is much smaller than that of the 1LO-phonon mode near resonance. Similar selectivity is also observed in other III-V compounds[5,6] and this high selectivity is characteristic of the **q** dependent Fröhlich interaction. The presence of compositional disorder enhances this type of interaction instead of weakening it,[6–8] which is evident from the anomalous enhancement in the intensity of the 2LO-phonon mode.

Concentration fluctuations can also localize an exciton. Defects (impurities, vacancies) and alloy-induced disorder in a crystal are the main mechanisms for localization. The localized exciton couples strongly to the most energetic LO phonon and it is suggested that exciton–LO-phonon complex acts as an intermediate state in the Raman process. Configuration model calculations[2,3] indicate that large oscillator strength for second-order scattering is possible when the localized exciton interacts strongly with the LO-phonon system. The appearance of energy-shifted first-order Raman modes near resonance and the anomalous enhancement in the intensity of the 2LO-phonon mode is attributed to this localized exciton–LO-phonon complex. If alloy-induced disorder is the main mechanism for localizing excitons, then one would expect increasing localization of excitons with increasing disorder. In fact, the authors[2,3] have investigated the effect of disorder in ternary alloy semiconductors with a fixed concentration and small degree of disorder. These effects would be reflected in the resonant Raman spectroscopy. The position and the width of the resonant curves reflect the perturbation on electronic states involved in the Raman process.

The purpose of this paper is to make a comparative study of the alloying effect in $GaAs_{1-x}P_x$ ternary alloys. In order to ascertain the nature of the intermediate states involved in the Raman process, resonant Raman studies were carried out by temperature tuning of the band gap, the temperature being varied between 295 and 10 K, and by changing the concentration x. Resonance at $E_0(\Gamma)$ band gap is studied in these two samples. The first- and second-order resonances in $GaAs_{0.1}P_{0.9}$ and the first-, second-, and third-order resonances in $GaAs_{0.35}P_{0.65}$ are presented in this paper. Also, a

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comparative study of resonant Raman scattering in $GaAs_{0.1}P_{0.9}$ and $GaAs_{0.35}P_{0.65}$ is presented.

Our results show the appearance of the replica of the first-order Raman mode energy shifted to the high frequency region near resonance. Anomalous enhancement in the 2LO-phonon mode compared to the 1LO-phonon mode is observed. Furthermore, in $GaAs_{0.35}P_{0.65}$, the oscillator strength for the 2LO-phonon mode near resonance is found to be greater than that of the 1LO-phonon mode. Third-order outgoing resonance at two different temperatures is observed in $GaAs_{0.35}P_{0.65}$ indicating the coupling of the localized exciton to the most energetic LO phonon. The anomalous enhancement in the 2LO-phonon mode, and the replica effect are attributed to the localized exciton–LO-phonon complex. Increasing disorder is found to increase the localization of the exciton, which is evident from the increase in excitonic lifetime, its binding energy, and the decrease in excitonic linewidth. Furthermore, the first-order resonance is found to have contributions from both band-to-band transition as well as localized excitons, while the second- and third-order resonances are found to have a contribution only from localized excitons.

II. EXPERIMENTAL PROCEDURE

The basic Raman spectroscopic system used for resonant Raman experiments consists of a RAMANOR double monochromator (HG2S), a HAMAMATSU R9493-02 photomultiplier tube, and an amplifier and discriminator, a photon counter, a chart recorder, and a light source (argon-ion laser, COHERENT, INNOVA 90-5). Resonant Raman experiments were carried out in a backscattering geometry, employing the different discrete lines of the argon-ion laser. The $Ga_{1-x}P_x$ alloys, with $\langle 100\rangle$ orientation and 60-μm epitaxial layer thickness, grown by the liquid-phase-epitaxy (LPE) technique, were obtained from Society Radio Technique Complete, Caen, France. The concentration x in these materials was accurately determined by electron microprobe analysis and photoluminescence with an accuracy better than 3%. The resonance effect is achieved by temperature tuning of the band gap of the material. The effect of tuning the temperature is equivalent to changing the photon energy of the laser by an amount equal in magnitude and opposite in sign to the corresponding change in band gap.[9] The resonant Raman experiments on these samples were performed by fixing the samples on the cold finger of a cryostat using silver paste, and the temperature of the order of 10 K was achieved using a HELITRON closed-cycle liquid-He cryostat. The temperature of the sample was measured accurately by keeping a thermocouple on the cold finger. In order to avoid condensation near the sample during the low-temperature experiments, the cryostat was evacuated to 1×10^{-6} torr by a typical ALCATEL rotary-diffusion pump combination. The double monochromator was calibrated with the strong plasma lines of the argon-ion laser. When the excitation energy is close to the absorption band edge of the sample, the measured intensity will be considerably weak, compared to the true scattered intensity. The observed intensity should be corrected for absorption before analysis. The corrected Raman intensity, at resonance, of these samples was obtained by including absorption correction, and by normalizing the measured intensity of the sample with the measured intensity of a reference scatterer, which in our case, was the 520-cm^{-1} line of silicon. Such a normalization corrects for the ω^4 dependence of the scattering cross section and also corrects for the wavelength dependence of the laser output power and of the system response. The lowest band gap of the samples investigated here is indirect, thus preventing masking of the Raman modes by luminescence near resonance.

III. RESULTS AND DISCUSSION

A. Exciton localization: Theoretical background

A simple atomistic model has been proposed by Balkanski *et al.*[2] to consider localized electronic states in alloy semiconductors introduced by concentration fluctuations. Concentration fluctuations can localize an exciton[2,10–12] and it has been suggested[2] that the intermediate electronic state in resonance Raman scattering is an exciton–LO-phonon complex, due to the strong coupling of the localized exciton to the most energetic LO-phonon. The configuration model calculations,[2] based on the excitonic localization concept, give expressions for the intensities of the 1LO, 2LO, and 3LO modes, which are given as

$$I(1\mathrm{LO})=A\left[\frac{z^2(1-z^2)^2}{[\hbar\omega_i-\hbar\omega(\mathrm{LO})-\varepsilon_0']^2+\Gamma^2}\right], \tag{1}$$

$$I(2\mathrm{LO})=\frac{A}{2}\left[\frac{z^4\left(1-2z^2+\frac{z^4}{2}\right)^2}{[\hbar\omega_i-\hbar\omega(2\mathrm{LO})-\varepsilon_0']^2+\Gamma^2}\right], \tag{2}$$

$$I(3\mathrm{LO})=\frac{A}{6}\left[\frac{z^6\left(1-3z^2+\frac{3z^4}{2}-\frac{z^6}{6}\right)^2}{[\hbar\omega_i-\hbar\omega(3\mathrm{LO})-\varepsilon_0']^2+\Gamma^2}\right], \tag{3}$$

where ε_0' is the excitonic energy level, Γ is the width of the localized exciton, $z=V/\hbar\omega(\mathrm{LO})$, where V is the coupling constant of the localized exciton to the LO phonon, $\hbar\omega_i$ is the incident photon energy, and $\hbar\omega(\mathrm{LO})$, $\hbar\omega(2\mathrm{LO})$, and $\hbar\omega(3\mathrm{LO})$ are the first-order second-order, and third-order phonon energies, respectively. A is the normalization constant. Similarly, the contribution to the Raman intensity from the transition across the direct band gap, based on Loudon's model, is given by

$$\begin{aligned}A(\omega_i)\approx\frac{1}{\omega_0}\Bigg\{&\sin\frac{\theta}{2}[(\omega-\omega_g)^2+\Gamma^2]^{1/4}-\sin\frac{\theta'}{2}[(\omega-\omega_0\\&-\omega_g)^2+\Gamma^2]^{1/4}\Bigg\}+\frac{i}{\omega_0}\Bigg\{\cos\frac{\theta}{2}[(\omega-\omega_g)^2+\Gamma^2]^{1/4}\\&-\cos\frac{\theta'}{2}[(\omega-\omega_0-\omega_g)^2+\Gamma^2]^{1/4}\Bigg\},\end{aligned}$$

where $\theta=\tan^{-1}[\Gamma/(\omega-\omega_g)]$ and $\theta'=\tan^{-1}[\Gamma/(\omega-\omega_0-\omega_g)]$. Here, ω is the incident energy, ω_g is the direct-band-gap value, ω_0 is the phonon energy, and Γ is the linewidth of the band-to-band transition.

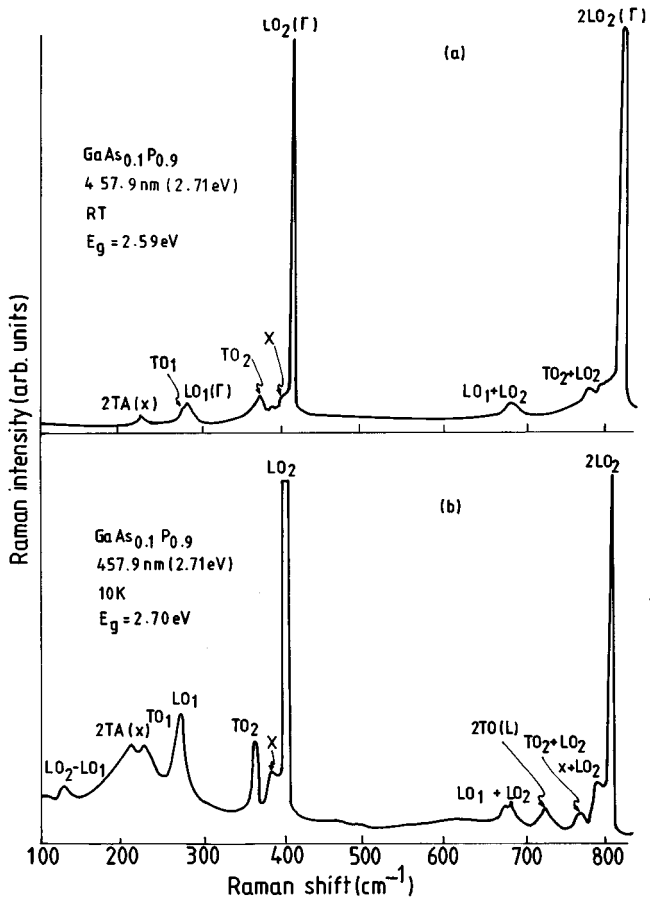

FIG. 1. Unanalyzed Raman spectrum of $GaAs_{0.1}P_{0.9}$ recorded with 457.9 nm (2.71 eV) (a) at room temperature and (b) at 10 K.

B. First-order resonance behavior

1. $GaAs_{0.1}P_{0.9}$

Figure 1(a) shows the unanalyzed room-temperature Raman spectrum of a LPE-grown $GaAs_{0.1}P_{0.9}$ alloy semiconductor with $\langle 100 \rangle$ orientation, recorded with the 2.71-eV line of the argon-ion laser. The room-temperature $E_0(\Gamma)$ band gap is 2.59 eV, and is 2.70 eV at 10 K. The $GaAs_{0.1}P_{0.9}$ crystal exhibits two-mode behavior, one corresponding to the GaAs-like LO-phonon mode and the other corresponding to the GaP-like LO-phonon mode. The first-order structures appear between 250 and 400 cm^{-1} and the second-order structures appear between 600 and 800 cm^{-1}, and around 210 cm^{-1}. Although the incident photon energy is above the $E_0(\Gamma)$ band-gap value, one can still observe residual resonance effect as evident from the appearance of the $2LO_2(\Gamma)$ mode. Figure 1(b) shows the unanalyzed Raman spectrum of $GaAs_{0.1}P_{0.9}$ recorded with the 2.71-eV line of the argon-ion laser at 10 K. Here, one can observe significantly richer structures between 600 and 800 cm^{-1} as compared to Fig. 1(a). One can also see the sharp and prominent appearance of the $2LO_2(\Gamma)$ model. These modes are the energy-shifted first-order Raman modes. An enhancement in the intensity of all the allowed modes is observed.

Figure 2 shows the resonance enhancement of the GaP-like first-order LO-phonon mode at 10 K. The experimental points were corrected for absorption. The experimentally observed sharp resonance for the $2LO_2$ mode indicates a dispersionless localized exciton as the intermediate state in the Raman scattering process, and for such a process the Raman intensity of the $1LO_2$-phonon mode (GaP-like) is given by Eq. (1). From the nature of the expressions for the Raman intensity of the $1LO_2$ mode and $2LO_2$ [Eqs. (1) and (2)], one would expect that the two intensities should have identical resonance behavior. Equation (2) is used to fit the resonance behavior of the $2LO_2$ mode, which will be discussed in a later section. The best fit is observed for $z=0.864$, $\varepsilon_0'=2.691$ eV, and Γ(excitonic)=20 meV. The same parameters are then used in Eq. (1) to fit the experimentally observed resonances behavior to the $1LO_2$ mode, which is shown in Fig. 2.

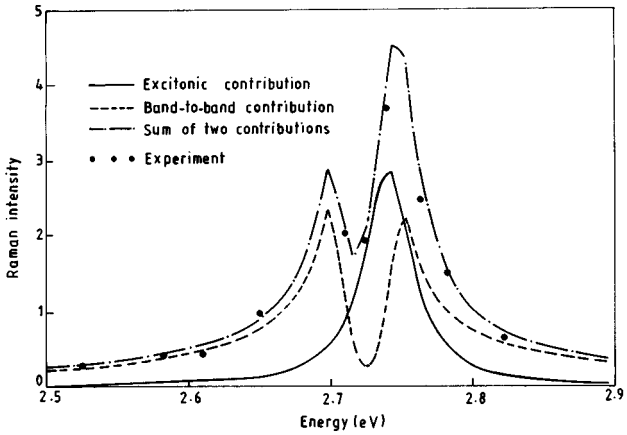

FIG. 2. Resonance behavior of the first-order GaP-like LO phonon in $GaAs_{0.1}P_{0.9}$ at 10 K.

From the figure, one can clearly see a large discrepancy between theory and experiment. This observation would automatically lead to a conclusion that there should be a contribution from other channels to the $1LO_2$-phonon scattering. The other channel for the resonance behavior is the resonance due to excitation across the direct band gap. The Raman amplitude for this process can be obtained from Eq. (4). Equation (4) is also used to fit the experimentally observed resonance behavior with $\omega_g=2.70$ eV and Γ (band-to-band)=10 meV, and the result obtained is also represented in Fig. 2. Now, one can see good agreement between theory and experiment when contributions to the enhancement in intensity from both the channels are included. The maximum value of intensity occurs when $\hbar\omega_i=2.740$ eV, for which the $1LO_2$-phonon energy lies 0.049 eV away from the excitonic energy $\varepsilon_0'=2.691$ eV, indicating an outgoing or scattered photon first-order resonance.

2. $GaAs_{0.35}P_{0.65}$

Figure 3(a) shows the unanalyzed room-temperature Raman spectrum of a LPE-grown $GaAs_{0.35}P_{0.65}$ alloy with $\langle 100 \rangle$ orientation, recorded with 2.41-eV line of the argon-ion laser. The $E_0(\Gamma)$ band in $GaAs_{0.35}P_{0.65}$ is 2.25 eV at room temperature and 2.36 eV at 10 K. This sample also exhibits two-mode behavior, one corresponding to the first-order GaAs-like LO-phonon mode, and the other corresponding to the first-order GaP-like LO-phonon mode. The first-order structures appear between 250 and 400 cm^{-1}, while the second-order structures in the high-frequency re-

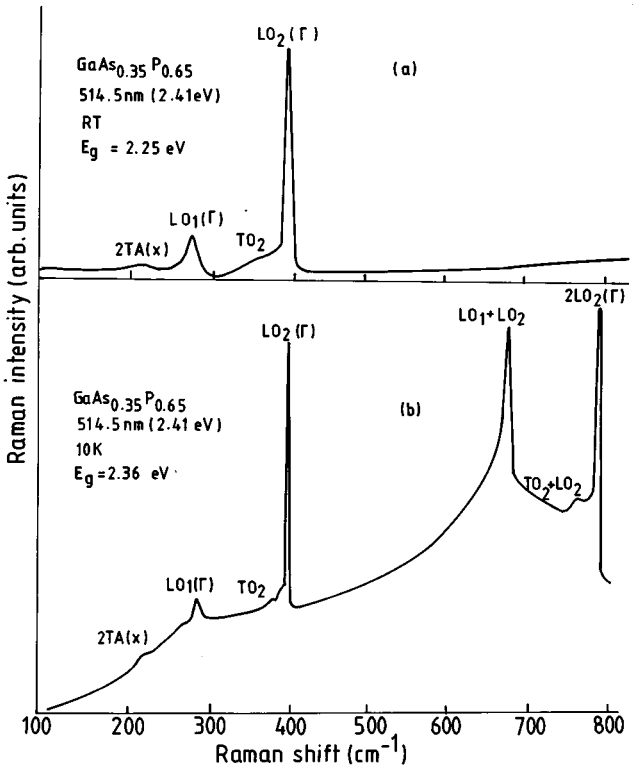

FIG. 3. Unanalyzed Raman spectrum of $GaAs_{0.35}P_{0.65}$ recorded with 514.5 nm (2.41 eV) (a) at room temperature and (b) at 10 K.

gion are completely absent, and the second-order transverse-acoustic mode at around 205 cm^{-1} appears as a very weak shoulder due to the presence of a high degree of disorder. Since the incident photon energy (2.41 eV) is far above the $E_0(\Gamma)$ band-gap value (2.25 eV), the resonance effect is not observed. Figure 3(b) shows the unanalyzed Raman spectrum of $GaAs_{0.35}P_{0.65}$ at 10 K recorded with the 2.41-eV line of the argon-ion laser. One can see the enhancement in the first-order GaAs-like, and GaP-like LO-phonon modes and the appearance of new modes in the high-frequency region between 600 and 800 cm^{-1}. The Raman spectrum of $GaAs_{0.35}P_{0.65}$ at 10 K is qualitatively different from the Raman spectrum of $GaAs_{0.35}P_{0.65}$ at 295 K. The high-frequency region between 600 and 800 cm^{-1} resembles that of first-order GaP-like optical phonons. Anomalous enhancement in the intensity of the LO_1+LO_2 mode and $2LO_2(\Gamma)$ mode is observed, compared to the intensity of the $1LO_2(\Gamma)$ mode. A selective resonance of the $2LO_2(\Gamma)$ mode is observed, even though the incident photon energy (2.41 eV) is not close to the $E_0(\Gamma)$ band-gap value (2.36 eV) at 10 K. The most important aspect of the Raman spectrum is the appearance of the Raman replica of the GaP-like modes between 750 and 800 cm^{-1}, even though the incident photon energy is not very close to the $E_0(\Gamma)$ band-gap value.

Figure 4 shows the resonance behavior of the GaP-like $1LO_2$-phonon mode at 10 K, where experimentally observed intensity of this mode was corrected for absorption. As discussed earlier, alloying introduces localized states in the forbidden band gap, which in turn creates a localized exciton–LO-phonon complex, and this complex gives rise to sharp resonance features. For such a process, the Raman intensity of the $1LO_2$ mode can be obtained by using Eq. (1). Equation (4) gives the contribution to the Raman intensity due to excitation across the direct band gap. Equation (1) with $z=0.900$, $\varepsilon_0'=2.342$ eV, and Γ(excitonic)=11 meV, and Eq. (4) with $\omega_g=2.36$ eV and Γ (band-to-band)=20 meV are used to fit the experimentally observed resonance behavior, which is shown in Fig. 4. Good agreement between theory and experiment is observed only when contributions from both exciton as well as band-to-band transitions are considered. The maximum value of intensity occurs when $\hbar\omega_i=2.390$ eV, for which the $1LO_2$ phonon energy is 0.048 eV away from the excitonic energy $\varepsilon_0'=2.342$ eV, indicating an outgoing scattered photon first-order resonance.

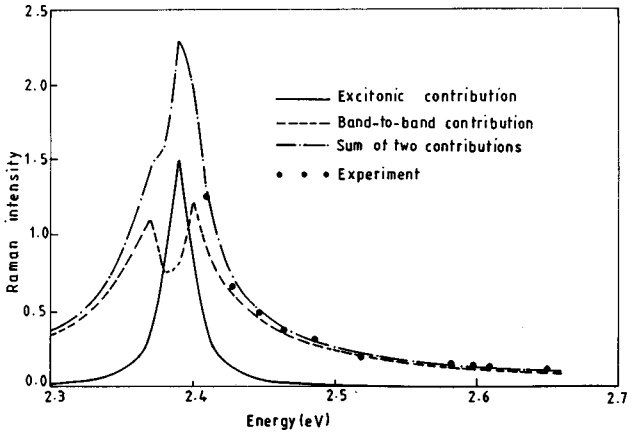

FIG. 4. Resonance behavior of the first-order GaP-like LO phonon in $GaAs_{0.35}P_{0.65}$ at 10 K.

C. Second-order resonance behavior

1. $GaAs_{0.1}P_{0.9}$

When the incident energy satisfies the condition $E_i=E_g+\hbar\omega(2LO)_2$, we observe second-order outgoing resonance. Figure 5 shows the evolution of the second-order spectrum in $GaAs_{0.1}P_{0.9}$ as a function of the incident photon energy and temperature. This spectrum is not normalized. It is evident from Fig. 5 that there is an enhancement in the intensity of the $2LO_2$ mode and, to some extent, of the LO_1+LO_2 mode. This behavior of the $2LO_2$ mode is anomalous, the enhancement being larger than that of the $1LO_2$ mode. Generally, the second-order structures are very sensitive to disorder. So, one would expect that the presence of disorder would lead to either weakening or complete disappearance of the second-order structure. But, on the other hand, a highly selective resonance of the $2LO_2$ mode is observed. However, away from resonance, the high-frequency region between 650 and 800 cm^{-1} consists of only residual second-order structures. Near resonance, the two-phonon spectrum disappears and an energy-shifted one-phonon spectrum appears.

The experimentally observed sharp resonance of the $2LO_2$ mode confirms that the localized exciton–LO-phonon complex acts as an intermediate state in the Raman scattering process. For such a process, the Raman intensity of the $2LO_2$ mode, based on the exciton localization concept, can be obtained from Eq. (2). Figure 6 shows the resonance behavior of the $2LO_2$ mode at 10 K. The resonance is already

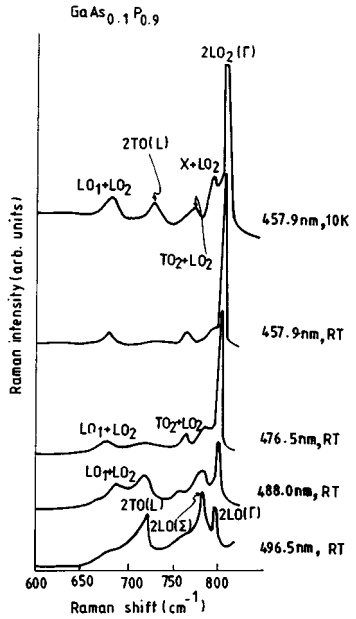

FIG. 5. Evolution of the second-order spectrum in $GaAs_{0.1}P_{0.9}$.

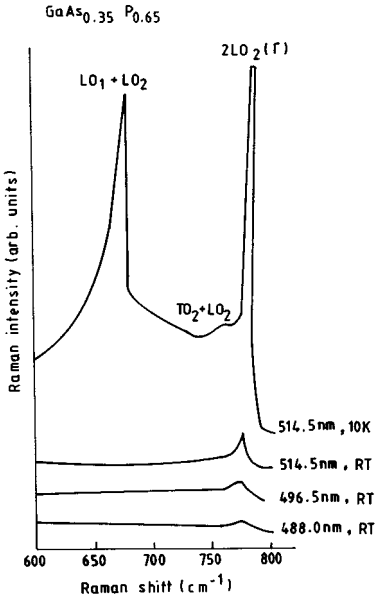

FIG. 7. Evolution of the second-order spectrum in $GaAs_{0.35}P_{0.65}$.

seen in Fig. 5 with the uncorrected data and the intensity increases further, which shows a large dispersion near the gap, when the experimental points are corrected for absorption. Equation (2) is used to fit the experimentally observed resonance behavior of the $2LO_2$ mode. The best fit between the theory and experiment is obtained for $z=0.864$, $\varepsilon_0'=2.691$ eV, and Γ(excitonic)$=20$ meV. For second-order resonance, the major contribution is from excitons only. It is also found that the contribution from band-to-band transition to the second-order resonance scattering, which is calculated using Eq. (4), is some two orders of magnitude less than the first-order resonance scattering. The maximum value of intensity takes place for $\hbar\omega_i=2.789$ eV for which the $2LO_2$ phonon energy lies 0.098 eV away from the excitonic energy $\varepsilon_0'=2.691$ eV, indicating an outgoing scattered photon second-order resonance.

2. $GaAs_{0.35}P_{0.65}$

Figure 7 shows the evolution of the second-order spectrum as a function of incident photon energy and temperature. Here, one can see that as the incident photon energy changes from 2.50 to 2.41 eV at room temperature, the $2LO_2$-phonon mode starts evolving. When the temperature is lowered to 10 K, a strong enhancement in the intensity of the $2LO_2$ mode occurs. Also, a considerable enhancement in the intensity of the LO_1+LO_2 mode is observed. The enhancement in the intensity of the $2LO_2$ mode is much greater than that of the $1LO_2$ mode near resonance, and also the $2LO_2$ mode resonance is much steeper than that of the $1LO_2$ mode. Because of the presence of a higher degree of disorder in this sample, one would normally expect that the second-order structures would either be weakened or totally disappear. The complete absence of the second-order structures in the high-frequency region between 600 and 800 cm^{-1} at 295 K confirms the above statement. When the incident photon energy is close to the $E_0(\Gamma)$ band gap, one observes, from Fig. 7, a highly selective resonance of the $2LO_2$ mode and, to some extent, the LO_1+LO_2 mode. This type of highly selective resonance may be attributed to the localized exciton–LO-phonon complex, which acts as an intermediate state in the scattering process. Disorder is the main mechanism for creating localized excitons, which couple strongly to the most energetic LO phonon and form a localized exciton–LO-phonon complex. Also, increasing disorder causes an increase in the localization of excitons. This is confirmed from the appearance of the anomalously enhanced and strong $2LO_2$ mode compared to the $1LO_2$ mode. For this type of process, the Raman intensity of the $2LO_2$ mode can be obtained from Eq. (2).

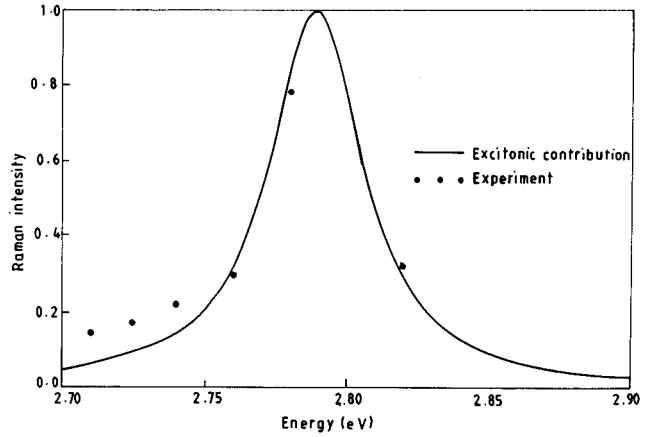

FIG. 6. Resonance behavior of the second-order GaP-like LO phonon in $GaAs_{0.1}P_{0.9}$ at 10 K.

Figure 8 shows the resonance behavior of the $2LO_2$-phonon mode at 10 K. The experimental points, which were corrected for absorption, are fitted by Eq. (2). A best fit between the theory and experiment is obtained for $z=0.900$, $\varepsilon_0'=2.342$ eV, and Γ(excitonic)$=11$ meV. For the second-order resonance, without including the contribution from band-to-band transition, good agreement between

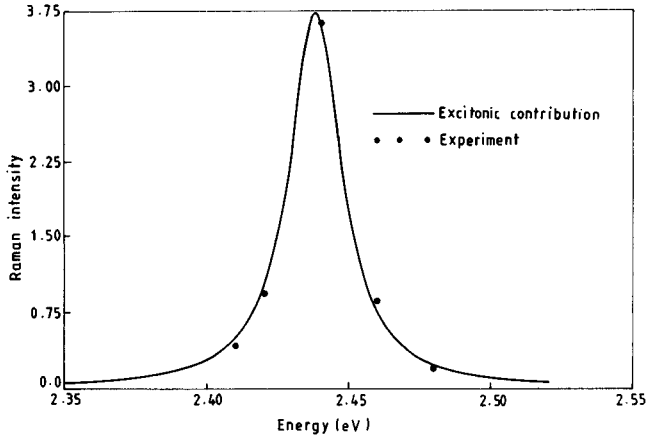

FIG. 8. Resonance behavior of the second-order GaP-like LO phonon in $GaAs_{0.35}P_{0.65}$ at 10 K.

theory and experiment is observed. It is also found that the contribution from band-to-band transition is some two orders of magnitude smaller than for the first-order resonance scattering. The maximum value of intensity occurs for $\hbar\omega_i = 2.440$ eV, for which the $2LO_2$ phonon energy lies 0.96 eV away from the excitonic energy $\varepsilon_0' = 2.342$ eV, indicating an outgoing scattered photon second-order resonance.

D. Third-order resonance behavior

1. $GaAs_{0.35}P_{0.65}$

When the incident energy satisfies the condition $E_i = E_g + \hbar\omega(3LO_2)$, we observe third-order outgoing resonance. Away from resonance, in the high-frequency region between 1100 and 1200 cm^{-1}, no third-order structure is observed, since the condition envisaged by the above statement is not satisfied. In $GaAs_{0.35}P_{0.65}$, third-order resonance is observed with the 514-5-nm line of the argon-ion laser at 200 K and with the 501.7-nm line of the argon-ion laser at 50 K. Figure 9 shows the evolution of the third-order spectrum recorded with 514.5 nm and 501.7 nm as a function of temperature. Both the spectra are not corrected for absorption, but the enhancement in the intensity is obvious when temperature is changed. In Fig. 9(a), no third-order structure is observed at room temperature. However, new modes appear between 1100 and 1200 cm^{-1} when the temperature is changed to 200 K, and these modes are attributed to an energy-shifted GaP-like first-order phonon mode. The intensities of these new modes start decreasing when the temperature is further lowered from 200 K, and at 130 K only a broad weak shoulder is observed. In Fig. 9(b), no third-order structure is observed between 1100 and 1200 cm^{-1} until 150 K. At 150 K, a small hump appears around 1180 cm^{-1}, which becomes sharper and prominent as the temperature is decreased further. At 50 K, one observes strong third-order structures which are energy-shifted GaP-like first-order phonon modes. When the temperature is decreased further, from 50 K down to 10 K, the third-order structures become weaker. The third-order structures, observed with 501.7 nm at 50 K, are comparatively strongly than the third-order structures observed with 514.5 nm at 200 K. These structures mainly contain a TO_2+LO_2 mode around 1160 cm^{-1} and a

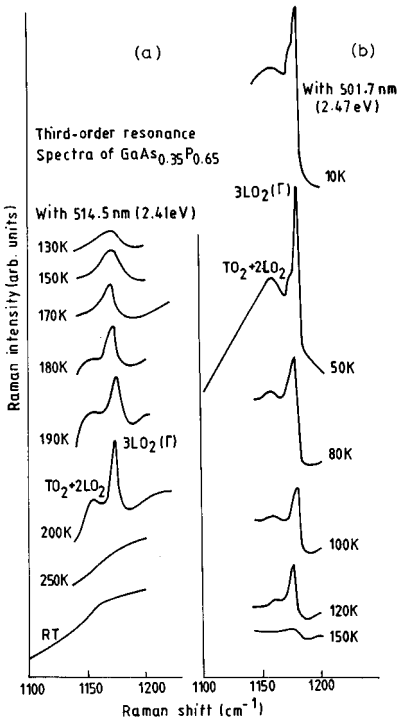

FIG. 9. Evolution of the third-order spectrum in $GaAs_{0.35}P_{0.65}$.

strong $3LO_2$ mode at 1180 cm^{-1}. Near resonance, one observes energy-shifted first-order GaP-like phonon modes. The replica effect is attributed to the localized exciton–LO-phonon complex as an intermediate state in the Raman scattering process. This type of scattering gives rise to sharp resonance features, which are, in fact, observed in the third-order resonance experiments. For such a process, the Raman intensity of the $3LO_2$-phonon mode, based on exciton localization concept, can be obtained by using Eq. (3).

Figures 10 and 11 show the resonance behavior of the $3LO_2$-phonon mode in $GaAs_{0.35}P_{0.65}$ at 200 K with 514.5 nm and 50 K with 501.7 nm. The experimental points, corrected for absorption, are fitted by Eq. (3). A best fit is obtained for $z = 0.900$, $\varepsilon_0' = 2.269$ eV, and $\Gamma(\text{excitonic}) = 11$ meV at 200 K, and for $z = 0.900$, $\varepsilon_0' = 2.342$ eV, and

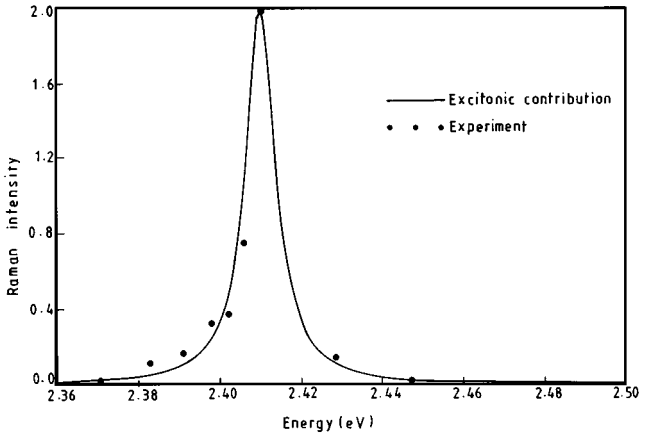

FIG. 10. Resonance behavior of the third-order GaP-like LO phonon in $GaAs_{0.35}P_{0.65}$ at 200 K.

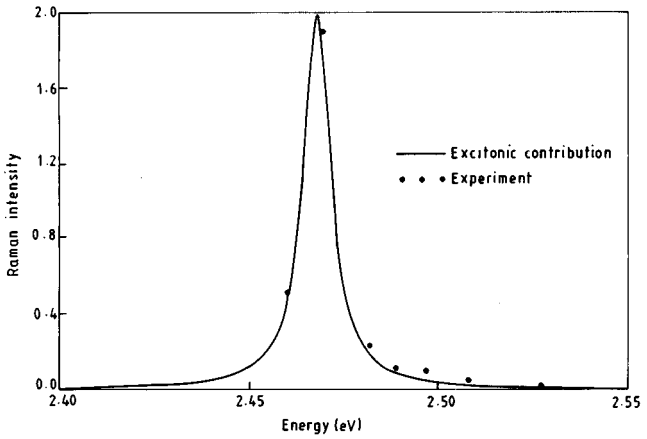

FIG. 11. Resonance behavior of the third-order GaP-like LO phonon in $GaAs_{0.35}P_{0.65}$ at 50 K.

Γ(excitonic)=11 meV at 50 K. Good agreement between theory and experiment is observed without including the contribution from band-to-band transition to the third-order resonance. As already discussed, the contribution to the second-order resonance from band-to-band transition is some two orders less in magnitude, compared to that for the first-order resonance, and for the third-order resonance, the contribution is still less and is therefore neglected. The maximum value of intensity takes place for $\hbar\omega_i=2.486$ eV at 50 K, for which the $3LO_2$-phonon energy is 0.144 eV away from the excitonic energy $\varepsilon_0'=2.342$ eV, and $\hbar\omega_i=2.413$ eV, for which the $3LO_2$ phonon energy is 0.144 eV away from the excitonic energy $\varepsilon_0'=2.269$ eV at 200 K, indicating the outgoing scattered photon third-order resonance.

E. Comparative study of resonant Raman scattering in $GaAs_{0.1}P_{0.9}$ and $GaAs_{0.35}P_{0.65}$ ternary alloy semiconductors

The scattered photon resonances of the first order and second order in $GaAs_{0.1}P_{0.9}$ and first order, second order, and third order in $GaAs_{0.35}P_{0.65}$ are discussed in the preceding sections. Equations (1) and (4) are used to explain the experimentally observed first-order resonance behavior and Eqs. (2) and (3) are used to explain the experimentally observed second-order and third-order resonance behaviors. The constants z, ε_0', and Γ(excitonic) are suitably chosen so as to have the best fit between theory and experiment. These constants z, ε_0', and Γ(excitonic) are the exciton-LO phonon coupling constant, excitonic energy, and excitonic linewidth, respectively. The effect of disorder in alloy semiconductors could be ascertained from the physical interpretation of these constants.

The exciton localization model assumes that alloying and alloy-induced disorder introduces localized electronic states. Otherwise, it is also possible that alloying could smear out the band edge. In the first case one would get sharp resonance features and in the latter case one would observe broadening of the resonance features. The assumption in the exciton localization model is confirmed from the sharp resonance feature observed in $GaAs_{1-x}P_x$ ternary alloy semiconductors. Also, configuration model calculations indicate that large oscillator strengths for the second-order scattering are possible when the localized exciton interacts strongly with the LO phonon system. This is also confirmed from the second-order resonance in $GaAs_{1-x}P_x$. If alloy-induced disorder is the main mechanism for localizing an exciton, one would expect that an increase in disorder would lead to an increase in localization. Table I gives the values of z, ε_0', and Γ(excitonic) for $GaAs_{0.1}P_{0.9}$ and $GaAs_{0.35}P_{0.65}$. In $GaAs_{0.1}P_{0.9}$, the localized excitonic energy state ε_0' is at 2.691 eV at 10 K and the $E_0(\Gamma)$ band gap value is 2.70 eV at 10 K. The difference between these two values $E_0(\Gamma)-\varepsilon_0'$ gives the binding energy of the exciton, which is 9 meV. The excitonic linewidth Γ(excitonic)=20 meV. If one uses the simple relation $\tau=h/\pi\Gamma$, the lifetime of the exciton is found to be 6.58 fs. In $GaAs_{0.35}P_{0.65}$, $\varepsilon_0'=2.342$ eV at 10 K and $E_0(\Gamma)=2.36$ eV. The binding energy of the exciton is found to be 18 meV. The excitonic linewidth is 11 meV, and the lifetime of the exciton is estimated to be 11.97 fs. The third-order resonances are observed at 200 K and at 50 K in $GaAs_{0.35}P_{0.65}$, and at these two temperatures, the excitonic binding energy is found to be 18 meV. From these values, one observes that as the disorder increases (when the phosphorus concentration decreases from 0.9 to 0.65), the binding energy of the exciton increases from 9 to 18 meV and the excitonic linewidth Γ(excitonic) decreases from 20 to 11 meV, which in turn increases the lifetime of the exciton from 6.58 to 11.97 fs. Also, as disorder increases, the coupling constant z, which couples the exciton to the most energetic LO phonon, increases from 0.864 for $GaAs_{0.1}P_{0.9}$ to 0.900 for $GaAs_{0.35}P_{0.65}$. This is also confirmed from the experimental observation in which a large oscillator strength for the second-order phonon mode, compared to the first-order phonon mode, is observed in $GaAs_{0.35}P_{0.65}$, compared to $GaAs_{0.1}P_{0.9}$, where the oscillator strength of the first-order and second-order phonon modes is almost equal, near resonance.

IV. CONCLUSION

A comparative study of alloying effect in $GaAs_{0.1}P_{0.9}$ and $GaAs_{0.35}P_{0.65}$ ternary alloy semiconductors, using resonant Raman spectroscopy, is presented. Alloying and

TABLE I. Values of the constants in Eqs. (1), (2), (3), and (4) for $GaAs_{1-x}P_x$ alloy semiconductors.

	$E_0(\Gamma)$ (eV)				ε_0' (eV)				Γ (band to band)	Γ (excitonic)	Life-
x	295 (K)	200 (K)	50 (K)	10 (K)	200 (K)	50 (K)	10 (K)	$E_0(\Gamma)-\varepsilon_0'$ (meV)	(meV)	(meV)	time (fs)
0.90	2.590			2.700			2.691	9	10	20	6.58
0.65	2.250	2.287	2.345	2.360	2.269	2.327	2.342	18	20	11	11.97

localized concentration fluctuations are found to be the main mechanisms for localizing an exciton, which couples strongly to the most energetic LO phonon to form a localized exciton-phonon complex. This complex acts as an intermediate state in the Raman scattering process, due to which an energy-shifted first-order phonon mode in the high-frequency region between 700 and 800 cm^{-1} and 1100 and 1200 cm^{-1} are observed in the Raman spectrum of $GaAs_{1-x}P_x$ alloy semiconductors. It is also confirmed that the localized exciton–LO-phonon complex is responsible for the sharp second-order resonance from the experimentally observed sharp resonance features. The localization is found to increase with increasing disorder (decrease in phosphorus concentration), which leads to an increase in the binding energy of the exciton and its lifetime. Increase in disorder also increases the coupling constant of the exciton to the LO phonon, which is confirmed from the strong oscillator strength for the second-order LO phonon, compared to the first-order LO phonon in $GaAs_{0.35}P_{0.65}$.

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