

## Raman-scattering probe of anharmonic effects in GaAs

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(Received 10 August 1994; revised manuscript received 28 November 1994)

A comparative study of anharmonic effects in various structural forms of GaAs, namely crystalline, disordered and ion-implanted, and pulse laser annealed (PLA), using temperature-dependent Raman scattering, is reported for various phonon modes over the temperature range 10–300 K. The disordered and PLA samples are found to have greater anharmonicity than crystalline GaAs. The localized vibrational mode in PLA GaAs shows shorter relaxation time than the LO-phonon mode.

### I. INTRODUCTION

Raman spectroscopy is a powerful technique for obtaining information about various vibrational modes in semiconductors. The Raman spectra corresponding to various modes of crystalline or amorphous materials show changes with temperature. These changes include a shift in line position and a change in linewidth and intensity. It is well known that the carrier relaxation rate, in general, is not dominated alone by the emission,<sup>1,2</sup> rather it is frequently dominated by the decay of strongly interacting optical phonons into weakly interacting acoustic phonons. Balkanski, Wallis, and Haro<sup>3</sup> and some other authors<sup>4,5</sup> have studied the temperature dependence of the optical modes at the center of the Brillouin zone for crystalline Si. They found that both the line center and linewidth vary with temperature due to anharmonic effects in the vibrational potential energy. Balkanski, Wallis, and Haro<sup>3</sup> have calculated the temperature dependence of the linewidth and line center for the first-order LO-phonon mode at the  $\Gamma$  point of the Brillouin zone, using second-order perturbation theory in the vibrational potential. They also performed experiments on a crystalline silicon sample and fitted their theory to experiments by suitably choosing the anharmonic constants involved. However, their studies are limited to the first-order zone-center LO mode of the crystalline silicon.

It is of some importance to relate information concerning the phonon relaxation processes obtained from an analysis of the broadening of Raman and infrared spectra to that obtained from other experiments. A more direct measurement of the lifetime of the LO phonon in the time domain, such as time-resolved spontaneous Raman scattering (TRSRS), can provide a detailed picture of the dephasing of molecular vibrations. Van der Linde, Kuhl, and Klingenberg<sup>6</sup> and Kash and Tang<sup>7</sup> used TRSRS to estimate the relaxation time of a nonequilibrium incoherent LO phonon generated during the interaction of photoexcited hot electrons and holes with the lattice for molecular beam epitaxy (MBE) grown GaAs. They typically observed a decrease in relaxation time with an increase in lattice temperature. Furthermore, Bhatt, Kim, and Strocio<sup>8</sup> have also estimated the lifetime of the LO phonon via anharmonic decay as a function of lattice temperature for bulk GaAs. They calculated the anhar-

monic crystal potential using a theory of elasticity based on Keating's treatment<sup>9</sup> of anharmonic contributions to the elastic strain energy of a crystal. They have also seen that the lifetime decreases with increasing temperature. As the third-order elastic constants used in their study were estimated at 300 K, the agreement at low temperatures may not be very good. Our analysis on the basis of temperature-dependent Raman-scattering experiments is in reasonable agreement with the published results.<sup>6–8,10</sup>

In an analogous fashion, we studied the temperature dependence of the Raman spectra in crystalline GaAs, ion-implanted GaAs, and pulse laser annealed (PLA) GaAs samples. We determined the anharmonic constants for GaAs, and our results show greater anharmonicity for GaAs than for Si. The temperature dependence of two-phonon Raman scattering is also discussed here with particular reference to the scattering involving two optic or two acoustic phonons. It is of interest to ascertain the behavior of anharmonic effects in highly disordered materials. For this study a GaAs sample, amorphized by phosphorus ion implantation, was used to obtain Raman spectra at various temperatures. The disordered GaAs shows a very strong temperature dependence. The ion-implanted sample was annealed using PLA, and Raman spectra for this sample was obtained at various temperatures. The Raman spectrum of this sample looks very similar to that of crystalline GaAs, indicating that the crystallinity of an ion-implanted GaAs sample has been mostly restored after PLA. However, there is a small difference in the linewidth and line center for various phonons, indicating that the vibrational potential for the PLA sample was slightly different from that for crystalline GaAs. This sample exhibits greater anharmonicity compared to the crystalline GaAs sample. The temperature dependences of both one- and two-phonon modes have also been studied for the ion-implanted and PLA GaAs samples. At high implantation fluences, the phosphorus-ion-implanted, PLA GaAs sample shows a phosphorus-localized vibrational mode (PLVM) in the Raman spectrum. The temperature dependence of the linewidth and line center of the PLVM has also been studied, and our results show that temperature rate of change of linewidth for the PLVM is larger than that for the LO-phonon mode.

The purpose of this paper is to make a comparative

study of the temperature dependence of various structural forms of GaAs, namely crystalline, disordered, and ion implanted and PLA, using Raman spectroscopy. In the present paper, measurements of the Raman-scattering spectra for different types of GaAs samples are reported in the temperature range between 10 and 300 K. The temperature dependences of the linewidth and line center of the one-phonon LO mode at the center of Brillouin zone are analyzed in terms of the anharmonic effects. The temperature dependence of two-phonon optical modes is also discussed through anharmonic effects. The Raman line that corresponds to the two-phonon acoustic modes shows strong temperature dependence. This dependence is explained by employing the Bose-Einstein statistics. The temperature dependence of the PLVM for ion-implanted and PLA GaAs is also related to the anharmonic effects. The theoretical fits give a satisfactory agreement with the experimental results.

## II. EXPERIMENTAL PROCEDURE

Raman-scattering experiments were performed in a backscattering geometry at different temperatures by employing the 496.5-nm wavelength of the argon-ion laser, the RAMANOR double monochromator, and photon-counting electronics. The (100) face of a 350- $\mu\text{m}$ -thick semi-insulating GaAs sample with a resistivity of  $10^7 \Omega \text{ cm}$ , procured from SUMITOMO ELECTRIC, Japan, was used. Furthermore, a GaAs sample implanted with phosphorus ions and subsequently PLA was also used in the study. The GaAs sample was implanted with 70-keV P ions with a fluence of  $1 \times 10^{16}$  ions/ $\text{cm}^2$ , which has a distribution profile with a maximum around 600  $\text{\AA}$ . The PLA process was performed with the  $\lambda = 1.06\text{-}\mu\text{m}$  wavelength of a Q-switched Nd:YAG (yttrium aluminum garnet) laser with a pulse width of 90 ns and a repetition rate of 10 Hz. The beam was focused on the sample to a spot of 100  $\mu\text{m}$  to achieve a power density of 20  $\text{MW}/\text{cm}^2$ . The sample was scanned in X and Y directions, and the beam was shot at a step of 50  $\mu\text{m}$  to achieve a  $2 \times 2\text{-mm}^2$  uniformly annealed area. The molten layer during the annealing process with this wavelength has a depth comparable to the range of implantation. Raman-scattering experiments were performed on samples fixed on the cold finger of a helium cryostat using sliver paste, and the temperature was regulated down to 10 K from room temperature using a HELITRON closed-cycle liquid-He cryostat. The cryostat was evacuated to  $1 \times 10^{-6}$  Torr to avoid condensation of moisture on the sample at low temperatures. The monochromator was calibrated using strong plasma lines of the argon-ion laser, and for a better accuracy the slit width of the monochromator was reduced to 75  $\mu\text{m}$ . The instrumental error is calculated from the given specifications of the optics and the geometry of the double monochromator. For a slit width of 75  $\mu\text{m}$ , the instrumental error is less than  $0.6 \text{ cm}^{-1}$ . The temperature of the sample was measured accurately by mounting the thermocouple on the cold finger. Each spectrum was recorded three times and the average values of the linewidth and line center were taken. The instrumental line function was also deconvoluted from

these experimental values to obtain the true intrinsic phonon frequencies and widths. The instrumental line function is assumed to be Gaussian and is estimated using a strong plasma line of the  $\text{Ar}^+$  laser (the linewidth of the plasma is much smaller than the slit width). The true Raman line is Lorentzian. If the line center and linewidth of the Raman line are  $\omega_0$  and  $\Gamma$ , respectively, and if the Gaussian line corresponding to the instrumental line function has a width  $\Gamma'$ , then the experimentally observed intensity at any frequency  $\omega$  will be a convoluted value given by

$$I(\omega) = \int \frac{l}{(\omega' - \omega_0)^2 + (\Gamma/2)^2} \exp \left\{ -\frac{(\omega - \omega')^2}{(\Gamma'/2)^2} \right\} d\omega', \quad (1)$$

where  $l$  is a constant. To find the true Raman line, the experimentally observed values were deconvoluted. For each temperature,  $I(\omega)$  in Eq. (1) was plotted for  $\omega = 280\text{--}305 \text{ cm}^{-1}$ , choosing proper values of  $\omega_0$  and  $\Gamma$  such that the calculated line function exactly matches the experimentally observed line. These values of  $\omega_0$  and  $\Gamma$  give the true value for the Raman line center and linewidth, respectively. The slit width was increased to 500  $\mu\text{m}$ , to observe the weak two-phonon structures, thereby decreasing the spectral accuracy to  $\pm 4 \text{ cm}^{-1}$ . All Raman experiments were performed at five different temperatures 10, 70, 140, 220, and 300 K, using the  $\lambda = 496.5\text{-nm}$  line of an  $\text{Ar}^+$  laser. The probing laser penetration depth is about 550  $\text{\AA}$ , which ensures the Raman signal from the implanted and annealed layer only.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

### A. One-phonon LO mode

The line center and linewidth of the one-phonon LO mode are experimentally found to vary with temperature. Balkanski, Wallis, and Haro<sup>3</sup> explained this variation by the anharmonicity in vibrational potential, which leads to decay of an optical phonon into two, three, or more acoustic phonons, giving rise to cubic and quartic anharmonicities. According to their calculations, the temperature dependence of the linewidth and line center of the one-phonon LO mode at the center of the Brillouin zone can be written as

$$\Gamma(T) = A \left\{ 1 + \frac{2}{e^x - 1} \right\} + B \left\{ 1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right\} \quad (2)$$

and  $\omega(T) = \omega_0 + \Delta(T)$ , where

$$\Delta(T) = C \left\{ 1 + \frac{2}{e^x - 1} \right\} + D \left\{ 1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right\}, \quad (3)$$

where  $x = \hbar\omega_0/2k_B T$ ,  $y = \hbar\omega_0/3k_B T$ ,  $\omega_0$  is the intrinsic frequency of the LO-phonon mode, and  $A$ ,  $B$ ,  $C$ , and  $D$  are different anharmonic constants.

The experiments in the present work were carried out at temperatures well below the ambient which are smaller

than the Debye temperature for GaAs. In this case it is important to consider only the first bracket term in Eqs. (2) and (3), and the last bracket term can be neglected. The resultant equations are used in the present study to explain the temperature-dependent variations in the linewidth and line center.

### 1. Crystalline GaAs

The average experimental values of the linewidth and line center for the one-phonon LO mode in the Raman spectra of crystalline GaAs at each temperature are plotted in Fig. 1. Equations (2) and (3) have been used to fit this experimental data by suitably choosing the constants  $\omega_0$ ,  $A$ , and  $C$ , which are given in Table I. Figure 1 shows that the agreement between the calculated curve, given by the solid line, and the experimental points is quite good. Table I also includes the values of the constants  $\omega_0$ ,  $A$ , and  $C$  for silicon given by Balkanski, Wallis, and Haro.<sup>3</sup> This shows that both the anharmonic constants  $A$  and  $C$  are numerically greater for GaAs than for Si, indicating that GaAs has greater anharmonicity.

Balkanski, Wallis, and Haro<sup>3</sup> calculated the matrix elements, which give interactions for various three- and four-phonon processes. These elements describe the anharmonic processes. Equations (2) and (3) are derived from these matrix elements using complicated derivations. However a simple macroscopic calculation given by Klemens<sup>4</sup> can be used to understand the temperature-dependent broadening and the anharmonic constant  $A$ , which is related to the linewidth in Eq. (2). The linewidth is related to the lifetime of the decay process of the involved phonon, and thus the constant  $A$  can be related to the lifetime of the decay process. For the temperatures used in the present study, we can assume that the LO phonon decays into two acoustic phonons. The relaxation time  $\tau$  for the anharmonic decay can be defined as proportional to the inverse of rate of change of the occupation number  $N$  of the mode, that is

$$\frac{1}{\tau} \propto \frac{dN}{dt}$$

In terms of the lattice parameter,  $a$ , Grüneisen parameter  $\gamma$ , velocity of the acoustic mode  $v$ , and the atomic mass  $M$ , the relaxation time<sup>4</sup> is written as

$$\frac{1}{\tau} \propto \frac{1}{M} a^3 \gamma^2 \left( \frac{\omega_0}{v} \right)^5 \quad (4)$$

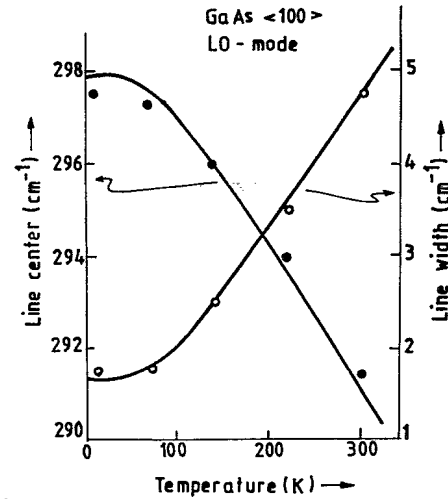


FIG. 1. Temperature dependence of the LO-phonon linewidth and line center for crystalline GaAs.

The atomic mass  $M$  can be replaced by the reduced mass  $\mu$  in the case of a diatomic molecule like GaAs. By substituting the values of these parameters for silicon and for GaAs in Eq. (4), we get

$$\frac{\tau_{\text{Si}}}{\tau_{\text{GaAs}}} = 1.30,$$

which matches quite well with our experimental results

$$\frac{A_{\text{GaAs}}}{A_{\text{Si}}} = 1.29,$$

confirming the inverse relation between the lifetime and the anharmonic constant  $A$ .

At lower temperature, the thermal agitation decreases, giving rise to an increase in the phonon mean free path, and so the decay lifetime increases. This leads to a decreased linewidth at low temperatures. Assuming the deconvoluted line shape to be Lorentzian, we can use the simple relation  $\tau = 1/(\pi c \Gamma)$  to estimate the relaxation time for the decay process, where  $c$  is velocity of light and  $\Gamma$  is the linewidth. This gives  $\tau = 2.2 \pm 0.2$  ps at 300 K, and  $6.5 \pm 1.8$  ps at 70 K. The relaxation times calculated or estimated by methods<sup>6-8,10</sup> other than Raman spectroscopy are typically around 3.5 ps at 300 K and 6.5 ps at 77 K. Raman scattering, being an indirect method, does not give very accurate value of  $\tau$  compared to a direct method such as the TRSRS. A more accurate

TABLE I. Numerical values of various anharmonic constants.

Sample	Phonon mode $\omega_0$	$\omega_0$ (cm <sup>-1</sup> )	$A$ (cm <sup>-1</sup> )	$C$ (cm <sup>-1</sup> )
Si <sup>a</sup>	LO	528.0	1.295	-2.96
Crystalline GaAs	LO	301.5	1.67	-3.62
Ion-implanted and PLA GaAs	LO	301.5	2.26	-4.61
Ion-implanted and PLA GaAs	PLVM	362.0	5.42	-4.05

<sup>a</sup>Values taken from Ref. 3.

direct measurement of the phonon lifetime could be the coherent Raman scattering. Also, when decay channels other than  $LO \rightarrow LA + LA$  exist, each process further decreases the measured lifetime. In view of these possible contributions, our results are in reasonable agreement with the published results.

The lifetime of the phonon due to various decay processes may be described in terms of the imaginary part of the phonon proper self-energy. The real part of the self-energy, on the other hand, gives the shift in the phonon energy. It can be calculated using the interaction strength and the polarizability at different temperatures. For most of the semiconductors, the temperature dependence of the polarizability is such that the real part of the self-energy increases at lower temperatures. This gives phonon hardening at lower temperatures. The negative value of the anharmonic constant  $C$  supports the above statement.

## 2. Ion-implanted and PLA GaAs

The Raman spectrum of the ion-implanted, PLA GaAs sample looks very similar to that of crystalline GaAs with little changes in linewidth, position, and intensity of various phonon modes. A room-temperature Raman spectrum of crystalline GaAs shows the LO-phonon mode at  $291.5 \text{ cm}^{-1}$ , with a  $4.75\text{-cm}^{-1}$  linewidth. The same mode for ion-implanted, PLA GaAs appears at  $289 \text{ cm}^{-1}$  with a  $6.0\text{-cm}^{-1}$  linewidth at room temperature. The intensity of this mode is slightly diminished for ion-implanted, PLA GaAs. These changes are generally caused by the presence of an impurity (in the present case, it is P ions), incomplete recrystallization, and the inhomogeneous strain created by microcrystals. In the latter case, the shift and broadening are also accompanied by a large asymmetry in the line shape, which is not observed in our experiments. Thus the shift and broadening observed by us at room temperature are predominantly caused by the presence of P ions and the possibility of partial crystallinity. The vibrational potential of the ion-implanted, PLA system is different from that for a crystalline system, and so the anharmonicity is also expected to be different for the two systems. The implanted and annealed sample was used for its temperature-dependent Raman studies. The average values of the line center and linewidth for the LO-phonon mode in Raman spectra from the sample at different temperatures are shown by small circular points, and the solid lines show the best fits to the experimental results in Fig. 2, thereby allowing a choice of the constants  $\omega_0$ ,  $A$ , and  $C$ . The dotted curves are the best fits for crystalline GaAs. The best values of these constants for good agreement with experimental results are listed in Table I.

One can see from Table I that the anharmonic constants  $A$  and  $C$  are numerically greater for ion-implanted, PLA GaAs than for crystalline GaAs, which indicates that the former has greater anharmonicity. PLA restores the radiation damages created by ion implantation; however, the implanted ions act as impurities and occupy a substitutional or interstitial position. The impurity ions act as scattering points for an incoming phonon, and

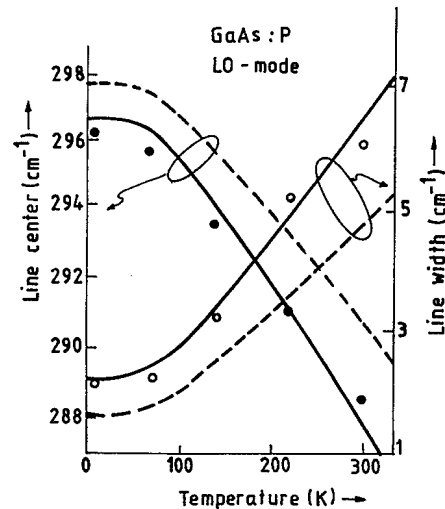


FIG. 2. Temperature dependence of the LO-phonon linewidth and line center for phosphorus-ion-implanted, PLA GaAs. The dotted lines show the temperature dependence for crystalline GaAs as in Fig. 1.

each scattering point promotes anharmonic decay of the LO phonon. A heavily implanted PLA sample thus has greater anharmonicity. This is experimentally seen in the form of faster temperature-dependent changes in the linewidth and line-center position for implanted and annealed GaAs than for crystalline GaAs. This is evident from Fig. 2, which shows greater slopes for solid curves than for dotted curves. The relaxation time for the decay of the LO phonon for a P-implanted, PLA GaAs is found to be about 1.8 ps at 300 K and 4.7 ps at 70 K.

## B. Two-phonon optical mode

Two-phonon optical modes in the Raman spectrum of GaAs appear mainly in the form of three weak peaks between  $500$  and  $600 \text{ cm}^{-1}$ , and are the overtones of optical modes. This type of second-order line spectrum is due to scattering involving two successive first-order processes. The line nature of the second-order scattering is the result of wave-vector conservation in two successive first-order Raman scatterings, and so the vibrational energy of these modes is also sum of the vibrational energies of the two first-order phonons. Therefore the temperature shift of the two-phonon structure is also the sum of shifts in two one-phonon modes.

The temperature shift and broadening for these modes cannot be observed with the same accuracy as was seen for one-phonon modes, because these modes are observed with greater slit widths. However, as the shifts in these modes are about  $12\text{--}14 \text{ cm}^{-1}$  when the temperature is lowered from room temperature to 10 K, a qualitative trend of shift can be observed. No mathematical equation has been fitted for the shift and broadening due to the loss in experimental accuracy. However, experimental results show that the shift at any temperature in the two-phonon line center is almost twice as much as that for the first-order spectrum, and the linewidth is almost the same as the width for the first-order mode at the same temperature. The dotted and solid lines in Fig. 3 show

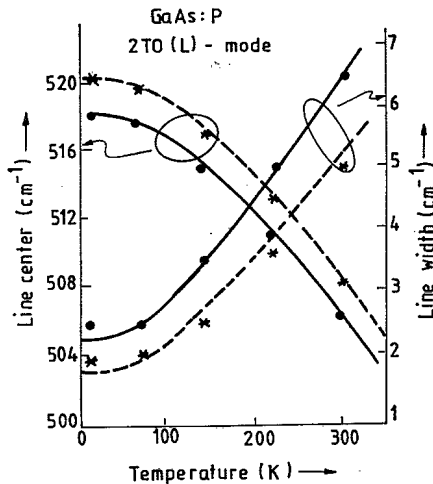


FIG. 3. Temperature dependence of the second-order optic phonon for crystalline and phosphorus-implanted, PLA GaAs samples, shown by dotted and solid lines, respectively.

the temperature dependence of the linewidth and line center for the two-phonon optical mode for crystalline GaAs and for ion-implanted, PLA GaAs samples, respectively. The dotted and solid lines are to guide the eyes. This figure shows that the two-phonon optical modes also show greater anharmonicity for ion-implanted, PLA GaAs than for a crystalline GaAs. As yet, according to our knowledge, no theory for the temperature dependence of the two-phonon process is available in the literature.

### C. Two-phonon transverse-acoustic mode

Figure 4 shows the weak second-order acoustic-phonon structure observed at increased slit width for a crystalline GaAs sample at different temperatures. This structure is due to overtones of the transverse-acoustic-phonon mode. The temperature-dependent changes in the broadening and line position fall within the instrumental error limits. However, Fig. 4 shows a strong temperature dependence on the intensity and overall structure of the two-phonon acoustic mode. The intensity of the mode decreases rapidly as the temperature is lowered. Thus the temperature-dependent changes could be studied only for the overall structure. This change cannot be due to any resonance effect, because we are far away from the resonance at these temperatures with the  $\lambda = 496.5$ -nm line of the  $\text{Ar}^+$  laser.

The number of phonons taking part in the scattering process can be determined by the intensity of the mode; however, if the mode is broad, it is proportional to the area under the mode structure. Due to the creation and annihilation of phonons at any finite temperature, the total number of phonons participating in the scattering process at any finite temperature is proportional to their occupation number. In terms of the Bose-Einstein function  $n_B$ , the occupation number can be written as  $n = 1 + n_B$ . For the two-phonon acoustic mode, the occupation number can be found at any temperature by substituting the value of  $\omega_0$  for that mode.

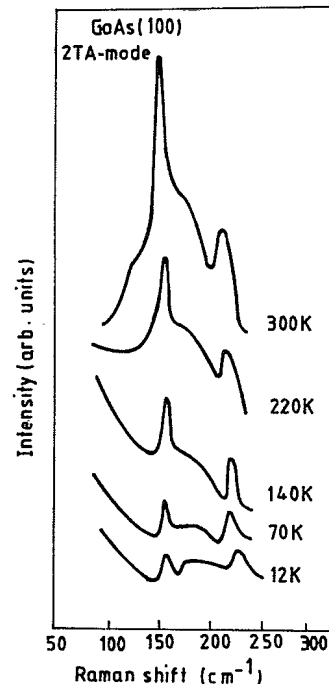


FIG. 4. Raman spectra of crystalline GaAs at different temperatures showing the 2TA mode.

### 1. Crystalline GaAs

Table II gives experimental values of areas under the mode structure at different temperatures for the 2TA mode for crystalline GaAs, and for phosphorus-implanted, PLA GaAs, in arbitrary units. It also gives the normalized values of areas. The normalized area  $A_n$  is calculated by  $A_n = PA + Q$ , where  $A$  is the area under the mode structure and  $P$  and  $Q$  are constants. The values of  $P$  and  $Q$  are properly chosen so that the value of  $A_n$  matches well with the theoretical value of the occupation number  $n$ . The solid curve in Fig. 5(a) shows the temperature dependence of the occupation number  $n$  at  $\omega_0 = 162 \text{ cm}^{-1}$ , and the points are the normalized values of area under the mode structure at different temperatures as given in Table II. This figure shows that the theoretical values of the occupation number  $n$  are in good agreement with the normalized experimental values of the area under mode structure.

### 2. Ion-implanted and PLA GaAs

PLA repairs the radiation damages; however, in a heavily implanted PLA GaAs sample, Raman scattering shows a decrease in the oscillator strength accompanied by a shift<sup>11</sup> in different Raman modes, compared to a crystalline GaAs sample. The 2TA mode is an overtone of a zone-edge phonon. The zone-edge phonons are more susceptible to any disturbance in the lattice structure than the zone-center phonons, and can be affected by small changes in the short-range order vibrational potentials. Thus the two-phonon acoustic mode has more of a changed structure for an ion-implanted, PLA GaAs sample than for a crystalline GaAs sample. Our spectra

TABLE II. Area under 2TA mode structure at different temperatures for crystalline GaAs and phosphorus-implanted, PLA GaAs.

Temperature (K)	Area under mode structure (arb. units)		Normalized area (arb. units)	
	Crystalline GaAs	Implanted and PLA GaAs	Crystalline GaAs	Implanted and PLA GaAs
10	17	12	0.96	0.94
70	19	13	0.99	0.97
140	40	34	1.25	1.27
220	64	57	1.55	1.59
300	87	76	1.84	1.81

show that the two-phonon acoustic mode for ion-implanted, PLA GaAs has a diminished oscillator strength and a slight shift in the peak position; however, the shift falls within the instrumental error. The experimental values of areas under this mode structure at different temperatures are also listed in Table II. The actual area of the sample given in Table II is different from the same given for crystalline GaAs sample, but the temperature-dependent changes are such that the normalized areas at different temperatures are almost the same for crystalline and ion-implanted, PLA GaAs samples, respectively. The temperature dependence of this mode for ion-implanted, PLA GaAs can also be explained by assuming  $n = 1 + n_B$ . Figure 5(b) shows experimental points and the theoretical fit with  $\omega_0 = 163 \text{ cm}^{-1}$ . The two theoretical curves in Figs. 5(a) and 5(b) are the same, as the normalized areas for the two samples are same.

#### D. Temperature dependence of PLVM

The PLVM in a phosphorus-ion-implanted, PLA GaAs appears near  $347 \text{ cm}^{-1}$  in the form of a line structure in a room-temperature Raman spectrum. This mode arises due to the localized vibrations of the impurity ions at the lattice site. The Raman spectra at different temperatures show a change in linewidth and line center for the PLVM. This temperature dependence of the linewidth and line center is very similar to the temperature dependence of the LO-phonon mode. This temperature variation can also be similarly attributed to the anharmonicity present in the vibrational potential for the localized vibrations. In this case, the local mode phonon splits into two acoustic phonons.<sup>12</sup> The main difference in the anharmonic decay of a LO phonon and local mode phonon is that in the first case one must consider momentum conservation, and in the other case the interaction is localized and there is no momentum conservation. The vibrational energy of the PLVM is extremely localized, extending generally over less than one lattice constant, therefore this mode is extremely sensitive to the short-range order disturbance. Due to extremely localized vibrations, the mean free path and the relaxation time are very short. This is experimentally seen in the form of a faster temperature dependence of the linewidth. Thus the constant  $A$  for this mode is expected to have a greater magnitude than that for the LO mode.

Equations (2) and (3) have been used for theoretical fits

to the experimental results. The best values of the constants  $\omega_0$ ,  $A$ , and  $C$  for good agreement with the experimental results for the PLVM are also listed in Table I. Here  $\omega_0$  can be treated as the intrinsic frequency of the PLVM, and the constants  $A$  and  $C$  give the anharmonicity in the vibrational potential associated with the PLVM. The anharmonic constant  $A$  has a much larger value for this mode than for the LO mode. The relaxation time for the decay of this localized mode is estimated to be about 0.85 ps at room temperature and about 1.9 ps at 70 K. This value is much smaller compared to those for the LO phonon. Thus the localized phonons are significantly short lived. The other anharmonic constant  $C$  is comparable to that for the LO mode. Figure 6 shows experimental values and theoretical fits for best values of anharmonic constants. Theoretical fits based upon anharmonic decay show good agreement with experimental values for the PLVM.

#### E. Disordered GaAs

The disordered GaAs sample is found to be much more sensitive to temperature than a crystalline or ion-

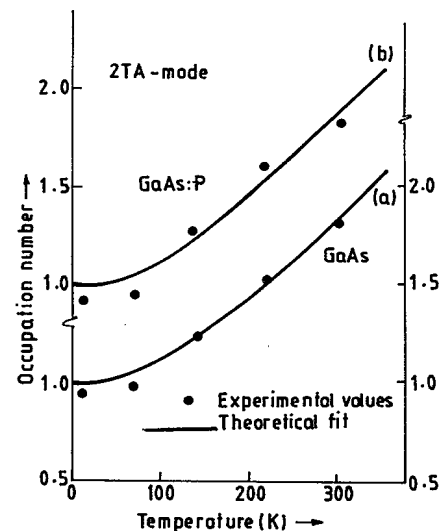


FIG. 5. Temperature dependence of the area under 2TA-mode structure for (a) crystalline GaAs and (b) phosphorus-implanted, PLA GaAs.

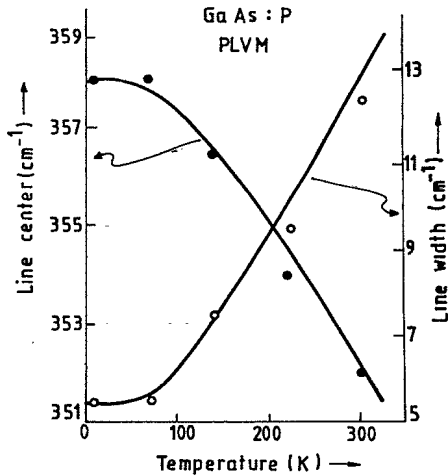


FIG. 6. Temperature dependence of the PLVM linewidth and line center for phosphorus-implanted, PLA GaAs.

implanted, PLA sample. The Raman spectrum of an amorphous GaAs sample has broad structures between 20 and  $300\text{ cm}^{-1}$ . The structure between 20 and  $100\text{ cm}^{-1}$  overlaps with the strong Rayleigh scattering at low temperatures. Figure 7 gives Raman spectra between 100 and  $300\text{ cm}^{-1}$  for a GaAs sample implanted with 70-keV phosphorus ions at a fluence of  $5 \times 10^{15}\text{ ions/cm}^2$ , at different temperatures. These spectra show the amorphous nature of the sample with a broad structure around  $250\text{ cm}^{-1}$  at room temperature. The intensity of this broad mode increases as the temperature decreases. As the temperature is lowered, along with the increase in intensity there is also a shift of the structure toward higher wave numbers. This structure has a broad peak near  $250\text{ cm}^{-1}$  at room temperature, which shifts to about  $270\text{ cm}^{-1}$  at 10 K.

This shift is almost three times greater than the shift observed in the LO phonon for a crystalline GaAs sample, due to the anharmonic effects. An amorphous material has considerable topological disorder and different kinds of defects. The short-range order defects become very important, and the sample becomes extremely sensitive to temperature. The large number of defects present in the sample act as scattering points, and each scattering point promotes a phonon to decay anharmonically. Thus the anharmonic effects in an amorphous material are very large, leading to such temperature-dependent shifts. The temperature effects in disordered materials are difficult to understand quantitatively. To our knowledge, no mathematical expression has been used in the literature to describe this temperature dependence.

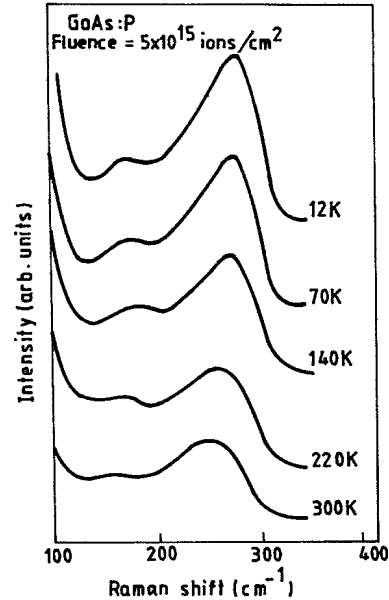


FIG. 7. Raman spectra of phosphorus-implanted GaAs for an implantation fluence of  $5 \times 10^{15}\text{ ions/cm}^2$  at different temperatures.

#### IV. CONCLUSION

A comparative study of temperature-dependent Raman scattering from the zone-center LO phonon shows greater anharmonicity for GaAs than Si. The anharmonic constants for crystalline GaAs are about 1.3 times greater than those for crystalline Si. The relaxation time for the decay of the LO phonon in GaAs varies from about 2.2 ps at room temperature to about 6.5 ps at 70 K.

A phosphorus-ion-implanted GaAs sample, well annealed using a pulse laser, exhibits partial crystallinity, as determined by changes in the linewidth and line center in the Raman spectra of crystalline and ion-implanted, PLA GaAs. Temperature-dependent Raman studies for one- and two-phonon scattering show that ion-implanted, PLA GaAs has almost 30% greater anharmonicity than crystalline GaAs. A completely disordered crystal of GaAs shows almost total topological disorder, leading to short-range order changes in vibrational potential. The Raman spectrum of this sample does not show any structure corresponding to zone-center phonons pertinent to long-range order. This sample is found to be highly sensitive to temperature, and the anharmonic shift is found to be almost three times greater than that for crystalline GaAs. The PLVM in ion-implanted, PLA GaAs has a small relaxation time, leading to a greater value of the anharmonic constant  $A$ , on account of localization of the vibrational potential.

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