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Local vibrational modes in GaAs under hydrostatic pressure

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Using infrared spectroscopy, we have observed local vibrational modes (LVM's) in GaAs at hydrostatic pressures as high as 7 GPa at liquid-helium temperatures. The shift of the infrared-active $v_3$vibrational mode of CO_2 impurities in the N_2 pressure medium was used as an *in situ* pressure calibration. We find that LVM's arising from $^{12}C_{As}$ and $^{13}C_{As}$ substitutional impurities vary linearly with pressure. The shifts of the $^{12}C_{As}$-H and $^{13}C_{As}$-H stretch modes have positive curvatures, while the pressure-dependent shift of the S-H stretch mode has a negative curvature. [S0163-1829(97)01236-8]

Local vibrational mode (LVM) spectroscopy is a useful technique for determining the microscopic structure of impurities and defects in semiconductors.[1,2] It has been widely used to investigate hydrogen-related complexes with excellent sensitivity,[3] since the hydrogen LVM frequencies lie well above the phonon frequency range. Hydrogen related LVM's can be unambiguously identified through the substitution of deuterium, which reduces the LVM frequency by a factor of $\sim\sqrt{2}$. After the discoveries that hydrogen passivates donors[4] and acceptors[5] in GaAs, numerous hydrogen-related complexes have been observed in compound semiconductors. In this paper, we report measurements of the dependence of hydrogen LVM's in GaAs upon large hydrostatic pressures.

The application of hydrostatic pressure is an excellent tool for probing the electronic and vibrational properties of defects in semiconductors.[6] Variable-pressure infrared-absorption spectroscopy has been used to study *X*-band donors in GaAs.[7] The pressure-induced transformation of the Si donor in GaAs from a hydrogenic to a *DX* state was observed directly by measuring the shift in the Si LVM.[8] In this study, we measured the shifts of the LVM frequencies of ^{12}C, ^{13}C, ^{12}C-H, ^{13}C-H, S-H, and S-D in GaAs as a function of hydrostatic pressure.

To generate pressures up to 7 GPa, we used a modified Merill-Bassett diamond-anvil cell.[9,10] Samples were cut into disks 300 μm in diameter and polished to a thickness of 50 μm. Nitrogen was used as a pressure medium and was loaded into the cell, along with the sample, using the liquid-immersion technique.[11] To determine the pressure at liquid-helium temperatures, we measured the infrared-absorption peak of the v_3 vibrational mode of CO_2 impurities in the N_2 matrix. The v_3 mode varies linearly with pressure[12] and provides a precise *in situ* calibration of the pressure.

Mid-infrared-absorption spectra were obtained with a Digilab FTS-80E vacuum Fourier-transform spectrometer with a KBr beamsplitter and a spectral range of 450–3400 cm^{-1}. The samples were kept at a temperature of 9 K in a Janis liquid-helium cryostat with KBr windows. The instrumental resolution was varied from 0.5 to 1 cm^{-1}, such that all the peaks were fully resolved. A light concentrating cone focused the light through the diamonds, the sample, and onto a Ge:Cu photoconductor mounted directly behind the sample.

GaAs:C epilayers were grown by metalorganic molecular-beam epitaxy on (100) semi-insulating GaAs substrates. After the growth of a 200 Å-thick buffer layer, they were carbon-doped from a beam of $^{12}CBr_4$ or $^{13}CBr_4$. The thicknesses of the GaAs:^{12}C and GaAs:^{13}C epilayers were 4 and 3 μm, respectively, and the free carrier concentrations were $\sim 10^{19}$ cm^{-3}. Additional details of the growth are given in Ref. 13. The samples were exposed to monatomic hydrogen in a remote plasma system.[14] The hydrogenation temperature was 350 °C and the duration of the exposure was 1 h. GaAs:S epilayers were grown by metalorganic chemical vapor deposition.[15] The thickness was 4 μm and the carrier concentration was 2×10^{18} cm^{-3}. The samples were exposed to a remote hydrogen or deuterium dc plasma for 50 h at a temperature of 180 °C.

In the GaAs:C, H complex, the hydrogen attaches directly to the carbon acceptor, in a [111] bond-centered orientation, adjacent to a host gallium atom. At atmospheric pressure and

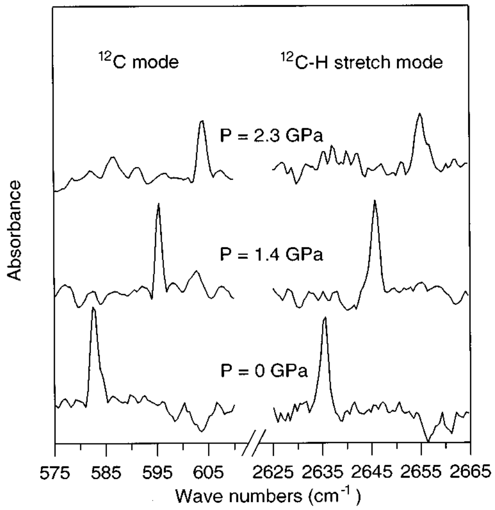

FIG. 1. Infrared-absorption peaks of ^{12}C mode and ^{12}C-H stretch mode in GaAs for different hydrostatic pressures at a temperature of 9 K.

liquid-helium temperatures, the ^{12}C-H and ^{13}C-H stretch modes have frequencies of 2635.2 and 2628.5 cm^{-1}, respectively. In our diamond-anvil cell samples, the weaker, lower-frequency *E* modes were not detected. In addition, the diamonds have intrinsic absorption bands from 1900 to 2200 cm^{-1}, precluding the measurement of ^{12}C-D and ^{13}C-D stretch modes.

The infrared-absorption spectra of the ^{12}C-H stretch mode and ^{12}C mode are shown in Fig. 1 for three different pressures. The ^{13}C-H stretch mode and ^{13}C mode are shown in Fig. 2. The peak positions are plotted as a function of pressure in Fig. 3. The substitutional carbon LVM's vary linearly with pressure, with least-square fits given by

$$v(^{12}\mathrm{C}_{\mathrm{As}}) = 582.7 + 9.31P, \tag{1}$$

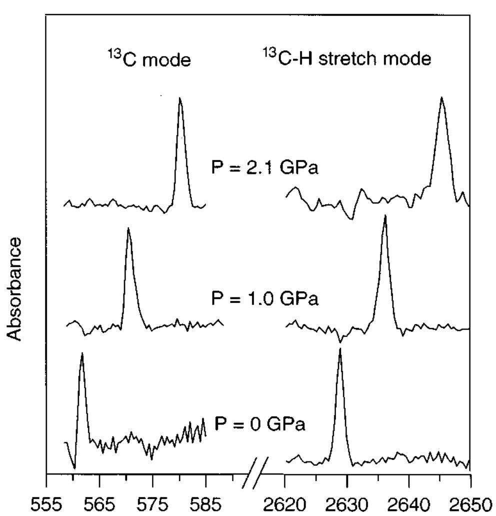

FIG. 2. Infrared-absorption peaks of ^{13}C mode and ^{13}C-H stretch mode in GaAs for different hydrostatic pressures at a temperature of 9 K.

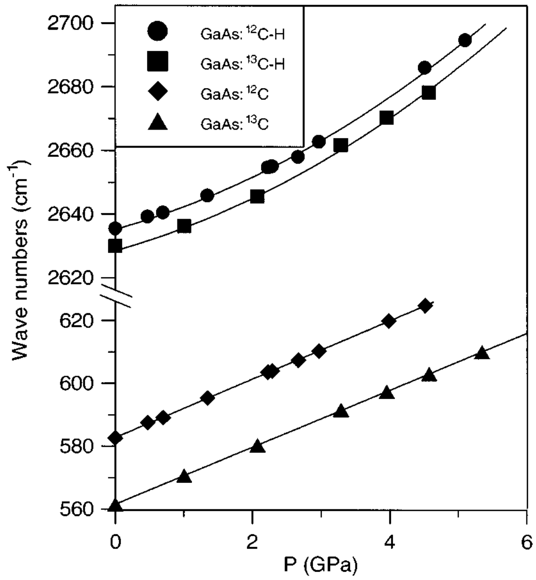

FIG. 3. Plot of C and C-H LVM's in GaAs as a function of hydrostatic pressure. The solid lines are fits to the data (see text).

$$v(^{13}\mathrm{C}_{\mathrm{As}}) = 561.5 + 9.08P, \tag{2}$$

where $v(^{12}\mathrm{C}_{\mathrm{As}})$ and $v(^{13}\mathrm{C}_{\mathrm{As}})$ are the LVM frequencies in cm^{-1} and P is in GPa. The plots of the hydrogen stretch modes as a function of pressure are nonlinear, with a positive curvature. Least-square quadratic fits yield

$$v(^{12}\mathrm{C}_{\mathrm{As}}\text{-H}) = 2635.2 + 6.0P + 1.1P^2, \tag{3}$$

$$v(^{13}\mathrm{C}_{\mathrm{As}}\text{-H}) = 2628.5 + 6.0P + 1.1P^2, \tag{4}$$

where the shifts of the two carbon isotopes are constrained to be equal. Since the $^{12}\mathrm{C}_{\mathrm{As}}$-H and $^{13}\mathrm{C}_{\mathrm{As}}$-H stretch mode frequencies only differ by 0.3%, the difference in pressure dependence cannot be resolved experimentally.

In group-VI donor-hydrogen complexes, the hydrogen is believed to bond with a host gallium in a [111] antibonding orientation. Since the hydrogen is isolated from the donor, its LVM frequency is very insensitive to the donor species, only varying $\sim$10 cm^{-1} from S to Te. We measured the pressure dependence of the S-H stretch and wag modes and the S-D wag mode. The S-D stretch mode was too weak to be detected in the diamond anvil cell sample. The infrared-absorption spectra of S-H stretch and wag modes are shown in Fig. 4 and the peak positions are plotted in Fig. 5. The S-H and S-D modes vary linearly with pressure, with least-square fits given by

$$v(\text{S-H wag}) = 781.0 + 7.7P, \tag{5}$$

$$v(\text{S-D wag}) = 556.6 + 5.3P. \tag{6}$$

The plot of the hydrogen stretch mode as a function of pressure is nonlinear, with a negative curvature. A least-square quadratic fit yields

$$v(\text{S-H stretch}) = 1512.3 + 11.6P - 0.52P^2. \tag{7}$$

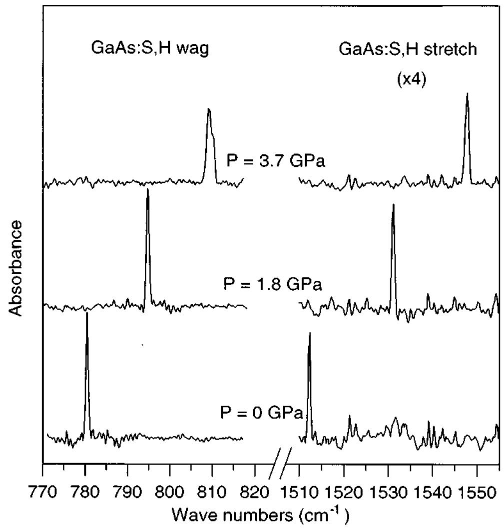

FIG. 4. Infrared-absorption peaks of hydrogen stretch and wag modes in GaAs:S,H for different hydrostatic pressures at a temperature of 9 K.

To compare these results, we use the mode Grüneisen parameter, defined as

$$\gamma_i = -\frac{\partial\omega_i/\omega_i}{\partial V/V} = \frac{B}{\omega_i}\left(\frac{\partial\omega_i}{\partial P}\right)_0, \tag{8}$$

where ω_i is the mode frequency, B is the bulk modulus, and the derivative is calculated at zero pressure. For GaAs, $B=75$ GPa.[16] The Grüneisen parameters for several LVM's in GaAs and AlSb are listed in Table I. It is interesting to note that the AlSb:Se,H and GaAs:S,H stretch modes have much different Grüneisen parameters, even though both centers are believed to have the hydrogen located in antibonding configurations.

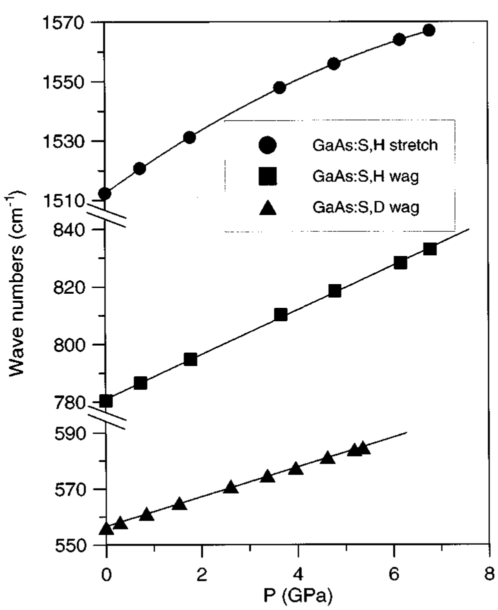

FIG. 5. Plot of S-H and S-D LVM's in GaAs as a function of hydrostatic pressure. The solid lines are fits to the data (see text).

TABLE I. Mode Grüneisen parameters for LVM's in GaAs and AlSb.

	Mode	γ
GaAs		
	^{12}Si[a]	1.29
	^{12}C	1.20
	^{13}C	1.21
	^{12}C-H stretch	0.17
	^{13}C-H stretch	0.17
	S-H wag	0.74
	S-D wag	0.71
	S-H stretch	0.58
AlSb		
	^{12}C[b]	1.28
	Se-H wag[c]	0.53
	Se-H stretch[c]	0.026

[a]Reference 8.
[b]Reference 12.
[c]Reference 19.

In summary, we have measured the pressure dependence of several LVM frequencies in GaAs. As in the case of AlSb:^{12}C (Ref. 12) and GaAs:^{28}Si,[8] we find that the ^{12}C and ^{13}C LVM frequencies vary linearly with pressure. The pressure-dependent shifts of the ^{12}C-H and ^{13}C-H stretch modes have positive curvatures, while the shift of the S-H stretch mode has a negative curvature. This may be related to the fact that in the bond-centered C-H complex, the hydrogen is compressed between the carbon acceptor and one gallium host atom, whereas in the S-H complex, the hydrogen occupies an interstitial position and is not crowded by neighboring atoms.

To explain the pressure dependence of the C-H stretch mode frequency, we approximate the potential of the hydrogen atom by

$$V(x) = kx^2/2 + A\,\delta(x - x_{\mathrm{Ga}}), \tag{9}$$

where k is the spring constant of the C-H bond, δ is the Dirac delta function, A is the strength of the perturbation, and x_{Ga} is the position of the host gallium atom. The δ-function perturbation shifts the LVM frequency by an amount

$$\Delta\omega = \frac{A}{\hbar\sqrt{\pi}}(2x_{\mathrm{Ga}}^2/a^2 - 1)e^{-x_{\mathrm{Ga}}^2/a^2}, \tag{10}$$

where $a = (\hbar/\sqrt{mk})^{1/2}$. For the C-H complex, $x_{\mathrm{Ga}} \gg a$ and Eq. (10) has a positive curvature with respect to x_{Ga}. Therefore, as the application of pressure linearly shortens the hydrogen-gallium distance x_{Ga}, the LVM frequency increases nonlinearly with positive curvature.

In the future, it would be of interest to explain the sublinear pressure dependence of the S-H stretch mode as well as the linear pressure dependence of the substitutional impurities. Although *ab initio* calculations have been performed for the structures of the C-H (Ref. 17) and S-H (Ref. 18) complexes, the pressure dependence of LVM's awaits a detailed theoretical treatment. If the trends found in this study are general, then variable pressure LVM spectroscopy may be used to determine whether other hydrogen-related complexes assume bond-centered or antibonding configurations.

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