

Local vibrational modes of carbon in GaSb and GaAsSb

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We have measured the Raman spectra of heavily carbon doped ($p > 10^{19} \text{ cm}^{-3}$) GaSb and GaAsSb. A local vibrational mode (LVM) due to carbon residing on group-V lattice sites was observed at 540 cm^{-1} for GaSb and 568 cm^{-1} for GaAs_{0.44}Sb_{0.56}. A gap mode at 164 cm^{-1} was observed for GaSb. The frequency of the LVM as well as the gap mode is in quantitative agreement with recent theoretical predictions. © 2002 American Institute of Physics. [DOI: 10.1063/1.1461871]

Antimony-containing materials are of increasing interest for both optoelectronic and electronic device applications. Cutoff frequencies in excess of 300 GHz have recently been observed in high-breakdown voltage InP/GaAsSb/InP double heterojunction bipolar transistors¹ using carbon as the GaAsSb base dopant. Extremely high hole concentrations can be achieved in carbon doped GaAsSb grown by metal-organic chemical vapor deposition (MOCVD) with very weak hydrogen passivation effects compared to MOCVD grown GaInAs. The high hole concentrations in C-doped GaAsSb suggest carbon is incorporated on group-V sublattice sites, but until now no independent confirmation of this assertion has been provided. Raman scattering from undoped GaAsSb has been reported in several studies^{2–4} however there are no prior reports of Raman scattering from carbon-doped GaAsSb or GaSb to our knowledge. Carbon has been extensively studied as a dopant for GaAs due to its very low diffusivity and high solubility. Local vibrational modes in GaAs and GaP due to carbon substituted for As or P have been reported in detail.^{5,6} In contrast carbon has received very little attention as a dopant for GaSb. Van Hove *et al.* demonstrated the use of a carbon *e*-beam source for *p*-type doping of molecular beam epitaxy (MBE) material to high levels ($p > 1 \times 10^{20} \text{ cm}^{-3}$).⁷ Carbon tetrachloride was recently demonstrated to be an effective carbon dopant for organometallic vapor phase epitaxy (OMVPE) growth of GaSb.⁸ In this work we identify local vibrational modes (LVM) for heavily carbon-doped GaSb and GaAsSb using Raman spectroscopy and compare the energies with recent theoretical predictions.

GaSb growth was performed in a vertical chamber at a growth temperature of 560°C on Te-doped GaSb (001) substrates (Ramet).⁸ GaAs growth was performed in a vertical chamber at a growth temperature of 560°C on GaAs (001) substrates (AXT). GaAsSb growth was performed at 560°C in a horizontal chamber using previously reported growth conditions on Fe-doped InP (001) substrates.⁹ Triethylgallium, tertiarybutylarsine, trimethylantimony, and carbon tetrachloride (500 ppm in hydrogen) were used as the precursors. Further details of the growth procedures have been reported elsewhere.^{8,10} Hall measurements were performed at

a field of 5000 G by the van der Pauw method, using In–Zn contacts alloyed under hydrogen at $250\text{--}300^\circ\text{C}$. The alloy composition of the heavily carbon doped GaAsSb sample was estimated from x-ray diffraction data, assuming coherent strain. From previous measurements of the effect of carbon on the lattice parameters of GaAs and GaSb in this laboratory we estimate that the actual Sb mole fraction of this sample is 0.561. Neglecting the effect of carbon on the lattice constant would give a Sb mole fraction of 0.547. Carbon concentrations were assumed to be equal to the measured acceptor concentrations.

The Raman spectra of GaSb and GaAsSb were measured with a triple spectrometer in a quasibackscattering geometry using the 488.0 nm line of an Ar-ion laser. The spectra of GaAs were measured using the 457.9 nm line which resulted in better signal-to-noise spectra because of a resonance effect.¹¹ Four polarization configurations were used in the Raman measurements, *XX*, *XY*, *X'X'*, and *X'Y'*, where *X*, *Y*, *X'*, and *Y'* refers to the [100], [010], [110], and $[\bar{1}10]$ crystal direction, respectively. For example, *XY* represents the scattering geometry in which the polarization direction of the incident light is along [100] and the polarization direction of the scattered light is along [010]. All the spectra were measured at an ambient temperature of 15 K. The estimated heating effect due to the incident laser is less than 20 K.

Figure 1 shows the Raman spectra of heavily carbon doped ($p > 10^{19} \text{ cm}^{-3}$) and undoped ($p = 6 \times 10^{16} \text{ cm}^{-3}$) GaSb samples. The undoped spectrum is dominated by the GaSb LO phonon at 240 cm^{-1} together with a weaker feature at about 450 cm^{-1} which we believe is due to two phonon processes and thus reflects the phonon density of states. The spectra of the heavily doped samples are dominated by a strong line at about 230 cm^{-1} which we attribute to the coupled hole plasmon-LO phonon mode, similar to published results for heavily *p*-type GaAs.¹² A careful examination reveals that the frequency of this coupled mode shifts from 231 to 225 cm^{-1} when the doping level is increased from 3.8×10^{19} to $1.5 \times 10^{20} \text{ cm}^{-3}$.

In the heavily carbon doped samples two additional narrow peaks, one at 164 cm^{-1} and the other at about 540 cm^{-1} , appear in *XY* and *X'X'* spectra. The Raman selection rules indicate that these are T_2 modes of the point group T_d .¹³ We attribute the 540 cm^{-1} mode to a localized vibra-

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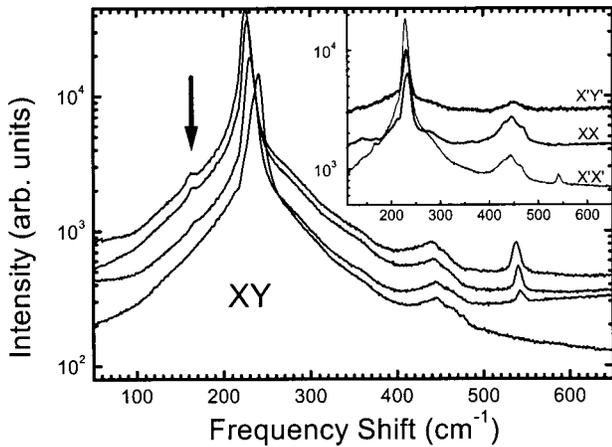


FIG. 1. Log plot of low temperature (15 K) Raman spectra of undoped and heavily carbon doped GaSb layers. From top to bottom: $p = 1.5 \times 10^{20}$, 6.7×10^{19} , 3.8×10^{19} , and $p = 6 \times 10^{16} \text{ cm}^{-3}$. Note the local vibrational mode at about 540 cm^{-1} and a gap mode at 164 cm^{-1} . The inset shows the spectra of heavily doped samples ($p = 6.7 \times 10^{19} \text{ cm}^{-3}$) measured in $X'Y'$, $X'X'$, and XX scattering geometries.

tion of substitutional carbon atoms on the Sb lattice sites, with bonding to four nearest-neighbor Ga atoms, similar to the well known LVM at 582 cm^{-1} observed in heavily carbon doped GaAs by IR and Raman spectroscopy.⁵ The decrease in the LVM mode frequency relative to GaAs primarily represents the effects of dilation of the C–Ga bonds due to the larger lattice constant of GaSb. Theoretical estimates of the carbon LVM mode energy in GaSb were previously reported by Robbie *et al.*¹⁴ assuming the same changes of force constant used to fit the GaAs local mode energies. With this approximation the LVM energy was calculated to be around 544 cm^{-1} . Robbie *et al.* further predict a gap mode at $\sim 166 \text{ cm}^{-1}$ assuming the same force constant changes. The gap between the acoustic and optical phonons in GaSb is very narrow, occurring from 161.4 to 182.9 cm^{-1} .¹⁴ Therefore, we attribute the 164 cm^{-1} mode observed in Fig. 1 to a carbon gap mode of GaSb. The present results show no evi-

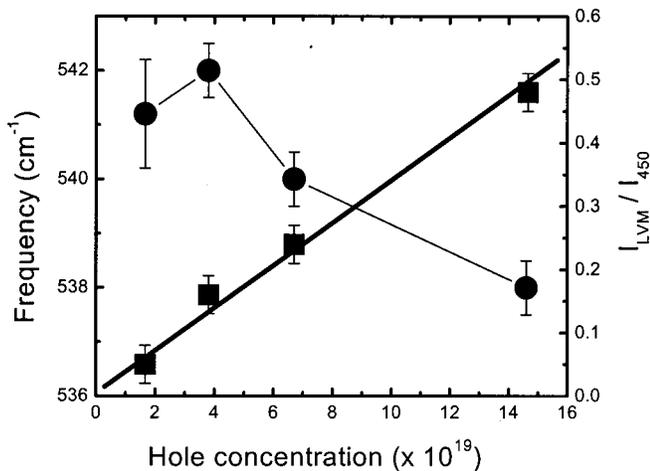


FIG. 2. Frequency and intensity of the LVM as a function of carbon doping level as measured by Hall effect. The solid circles represent the peak frequency. The squares represent the ratio of the integrated intensity of the LVM to that of the 450 cm^{-1} peak. The thick solid line represents a fit using Eq. (1).

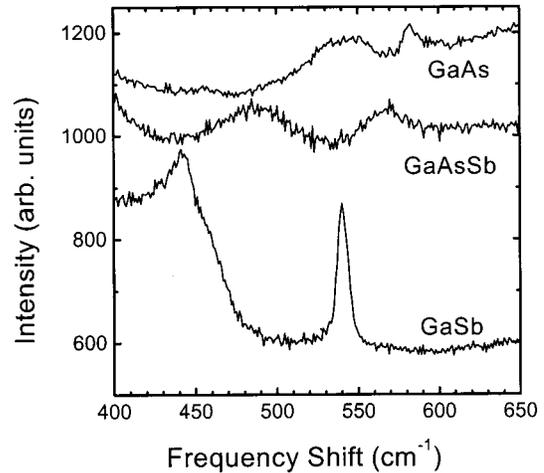


FIG. 3. Raman spectra of heavily carbon doped (from top to bottom) GaAs ($p = 7.5 \times 10^{19} \text{ cm}^{-3}$), $\text{GaAs}_{0.44}\text{Sb}_{0.56}$ ($p = 1.0 \times 10^{20} \text{ cm}^{-3}$), and GaSb ($p = 1.5 \times 10^{20} \text{ cm}^{-3}$), measured using XY scattering geometry.

dence of carbon on Ga sites, which would be expected to produce a LVM at lower energy than carbon on Sb sites.

Figure 2 shows the doping dependence of the frequency and intensity of the LVM in GaSb. When the doping level is increased from 3.8×10^{19} to $1.5 \times 10^{20} \text{ cm}^{-3}$, the LVM peak shifts towards lower frequency by $4 \pm 1 \text{ cm}^{-1}$. The effect of lattice parameter shift due to carbon-induced lattice contraction would be expected to shift the local mode energy to higher energies, opposite to the observed trend. On the other hand, a coupling effect between vibrational and electronic excitations could result in the observed redshift in frequency.¹⁵ This mechanism was invoked by Wagner *et al.* to explain a similar effect in Be-doped GaAs.¹⁶

In addition, we normalized the integrated intensity of the LVM to that of the second-order phonon Raman spectrum at 450 cm^{-1} . As shown in Fig. 2, the integrated intensity of the LVM increases linearly with increasing hole concentration as expected from the relation¹⁷

$$I_{\text{LVM}} \sim pV\sigma, \tag{1}$$

where p represents the hole concentration, V the scattering volume, and σ the scattering cross section per impurity.

Figure 3 shows a comparison of the LVM of heavily

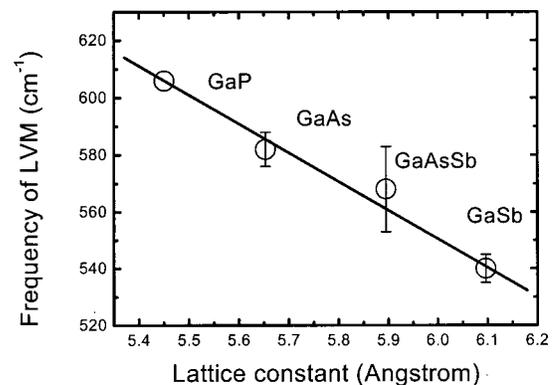


FIG. 4. Frequency of the carbon LVM vs lattice parameter for GaP, GaAs, GaSb and GaAsSb. For the GaAsSb sample we used the relaxed lattice constant as inferred from x-ray measurements. The error bar represents the linewidth (FWHM).

TABLE I. Summary of experimental values of the carbon local mode energies for various materials.

Material	Carrier concentration (cm ⁻³)	LVM energy (cm ⁻¹)	Linewidth FWHM (cm ⁻¹)
GaP	N/A	606 ⁶	N/A
GaAs	7.5 × 10 ¹⁹	582	12
GaAs _{0.44} Sb _{0.56}	1.0 × 10 ²⁰	568	30
GaSb	1.5 × 10 ²⁰	538 ± 0.5	10
GaSb	6.7 × 10 ¹⁹	540 ± 0.5	10
GaSb	3.8 × 10 ¹⁹	542 ± 0.5	10
GaSb	1.7 × 10 ¹⁹	541 ± 1.0	10

doped GaAs, GaAsSb, and GaSb samples. The frequency of the LVM of the ternary alloy GaAs_{0.44}Sb_{0.56} is 568 cm⁻¹, which is between the frequencies of the LVM in GaAs and GaSb. This confirms that the Ga–C bonding in C-doped GaAsSb is stronger than that in GaSb but weaker than that in GaAs as expected. As shown in Fig. 4, the frequency of the LVM linearly depends on the lattice constant in these materials. Furthermore, it is interesting to note that the linewidth of the LVM in GaAsSb is about three times as large as that of GaSb and GaAs. This broadening of LVM in the ternary alloy can be interpreted as the consequence of alloy effects. In particular, while the average lattice spacing in the GaAsSb sample is constant over large length scales, the interatomic distance can vary within a range, due to alloy or compositional fluctuations. As a result, the LVM mode for the alloy should be broadened. In addition, the mass distribution of the second nearest neighbor group-V atoms surrounding the carbon impurity should vary due to alloy disorder, which might have a contribution to the broadening of the LVM in the alloy.

Table I shows a summary of the relevant experimental values for the LVM measured in the present study as well as the commonly accepted values for GaP and GaAs for comparison.

In conclusion, we have identified local vibrational modes of carbon acceptors substituting for group-V sites in GaSb and GaAsSb heavily doped with carbon. Local and gap modes at 540 and 164 cm⁻¹ were identified for GaSb. A local mode intermediate between those of GaSb and GaAs was observed in GaAs_{0.44}Sb_{0.56}.

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