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Local vibrational mode study of carbon-doped InAs

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Carbon-doped InAs samples grown by organometallic vapor phase epitaxy were studied by Raman and IR spectroscopy. Local vibrational modes (LVMs) related to isolated substitutional carbon acceptors, carbon acceptor-hydrogen complexes, and dicarbon centers were detected in samples doped with two isotopes of carbon. The energies of the observed carbon-hydrogen modes are in close agreement with carbon acceptor-hydrogen modes in GaAs and InP, and are consistent with hydrogen occupying a bond-center position in the complex. No sign of substitutional carbon donors was observed. The n-type conductivity of carbon-doped InAs can be explained by the presence of dicarbon centers that are believed to be deep donors. The stretch mode of this complex was detected at 1832 cm^{-1} by Raman spectroscopy in as-grown and annealed samples.

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I. INTRODUCTION

Carbon has been widely used as an acceptor dopant for several III-V semiconductors. Because of its low diffusivity and high solubility, doping levels as high as 10^{20} cm^{-3} can be easily achieved. Local vibrational mode (LVM) studies of most III-V semiconductors such as GaAs, GaP, GaSb, and AlAs show that carbon occupies the group V lattice site in these materials and behaves as an acceptor. However, the case is different for two In-containing compounds InP and InAs. Carbon doping of these two materials makes them semi-insulating and n type, respectively.[1,2] In the case of InP, it had been assumed that carbon can be incorporated on the group III lattice site, i.e., as C_{In}, but the only spectroscopic evidence of carbon donors was limited to the observation of a gap mode at 220 cm^{-1} by Raman spectroscopy.[3] The assignment of this line to carbon donors was not conclusive because there was no correlation between the intensity of this line and the carbon concentration measured by secondary ion mass spectroscopy (SIMS). On the other hand, LVMs of C_{P} acceptors and H-C_{P} pairs were detected at 546.9 and 2703 cm^{-1} by Raman spectroscopy and IR absorption measurements.[4,5]

We have previously reported the observation of carbon and carbon-hydrogen related LVMs in InAs by Raman spectroscopy.[6] It was proposed that the detected carbon LVM is related to isolated substitutional acceptors, however, we were not able to explain the n-type conductivity of the layers at that time. In this paper we present the results of Raman spectroscopy and IR absorption measurements of ^{12}C- and ^{13}C-doped InAs samples grown by organometallic vapor phase epitaxy (OMVPE). It will be confirmed that carbon occupies the As lattice site as an isolated substitutional acceptor. Some of these carbon acceptors are passivated by hydrogen atoms occupying the bond-centered position, as in GaAs and InP. Also, it will be proposed that n-type conductivity of the layers can be explained by the presence of deep level dicarbon defects, similar to those identified in earlier works on GaAs and InP.

II. EXPERIMENT

InAs epilayers were grown on (001) oriented GaAs and InAs substrates in a vertical OMVPE reactor at a pressure of 50 Torr and substrate temperature of 375 °C. Layer thicknesses for IR samples were grown to approximately 1 μm, in order to maximize the absorption signal. Trimethylindium (TMIn), tertiarybutylarsine (TBAs), natural carbon tetrabromide (CBr_4), and carbon tetrachloride (CCl_4) with a mixture of 70% ^{13}C and 30% ^{12}C were used as the precursors. Growth rates were determined by high resolution x-ray diffraction measurements of samples grown on InAs substrates. A triple spectrometer in a quasibackscattering geometry using the 488.0 nm line of an Ar-ion laser with an excitation power of 60 mW focused on a line of 50×500 μm was used to measure the Raman spectra at room temperature and 25 K. IR absorption measurements were performed with a Bomem DA8 interferometer using a Mylar beamsplitter and a Si:B detector at 4.2 K for the low energy modes and a CaF_2 beamsplitter and InSb detector at 77 K for the higher energy modes. For both sets of measurements the samples were cooled by flowing He gas in a Varitemp Dewar, with polypropylene windows for the low-energy measurements and ZnSe windows for the high-energy region. The measured IR spectra do not represent the absolute absorbance of the samples.

III. RESULTS

A. LVMs of isolated carbon acceptors

Previously reported results of Raman measurements conducted at room temperature showed that ^{12}C doping of InAs gives rise to a LVM at 527 cm^{-1}.[6] Based on energy trends of carbon acceptors in other III-V semiconductors, it was concluded that this mode was due to isolated carbon acceptors on As lattice sites (T_d symmetry). In order to verify this assignment we performed Raman spectroscopy and IR absorption measurements on two sets of samples: the first one doped with natural C (∼99% ^{12}C) and the second one doped with a mixture of ^{12}C and ^{13}C.

Figure 1 shows the room temperature Raman spectra for samples doped with natural carbon [Fig. 1(a)] and carbon enriched in ^{13}C [Fig. 1(b)]. The previously observed ^{12}C peak at 527 cm^{-1} is present, along with an additional ^{13}C line at 508 cm^{-1}. The latter LVM is superimposed on the high-frequency edge of the broad 2LO peak. Figure 2 shows 25K

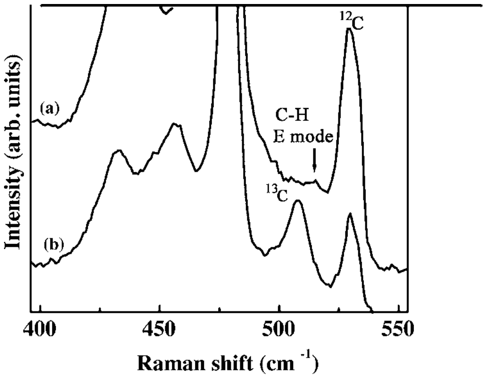

FIG. 1. RT Raman spectra of samples doped with ^{12}C and ^{12}C and ^{13}C.

IR absorption spectra in the same energy region as the previous Raman spectrum. The same two LVMs at wave numbers of 530.5 and 511 cm^{-1} are observed in the mixed isotope sample, along with other peaks that will be discussed in the following sections. The frequency of the IR peaks has been slightly shifted towards higher frequencies relative to the Raman peaks due to the lower measurement temperature. The ratio of the integrated absorptions of these two modes is approximately 30:70 consistent with the relative abundances of ^{12}C/^{13}C in the CCl$_4$ source. The isotopic frequency shift of $\nu(^{12}\mathrm{C})/\nu(^{13}\mathrm{C})=1.038$ is identical to that for InP:C$_\mathrm{P}$ and very close to the typical values for carbon acceptors in other III-V semiconductors.[7]

B. LVMs of carbon-hydrogen complexes

We have already reported the detection of a LVM in room temperature Raman spectra at 386 cm^{-1} that we attributed to a C-H complex.[6] The same mode was observed in IR absorption experiments at 393.2 cm^{-1} at 25 K (Fig. 3). Based on a comparison with accepted modes in GaAs and InP (see Table I), we attribute this mode to the low frequency longitudinal mode (A_1^+) of C-H, in which both atoms oscillate in phase, resulting in a lower energy mode than that of the isolated carbon acceptor. This mode is both IR and Raman active and its Raman scattering intensity shows strong resonant enhancement.[8] Therefore the rather strong appearance of this line in our Raman spectra[6] can be explained by the optical excitation energy (2.55 eV) that is very close to E_1 gap energy in InAs (2.61 eV).[9]

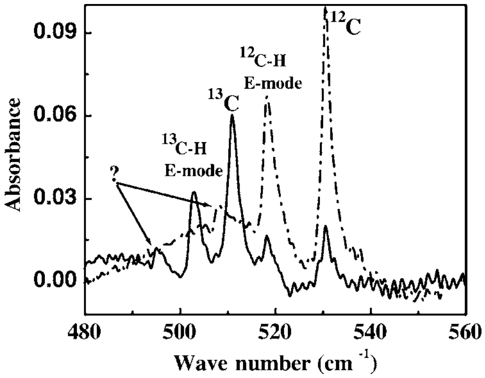

FIG. 2. IR spectra measured at $T=25$ K. The solid line represents the sample doped with both isotopes and the dash-dot line is for the sample doped with ^{12}C.

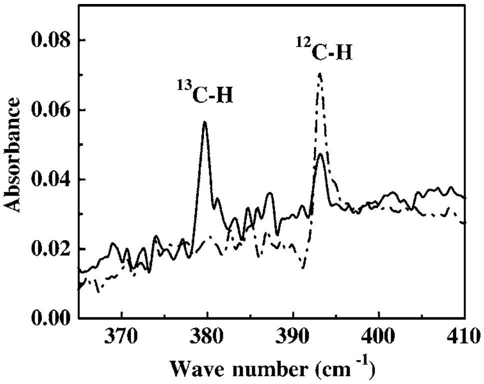

FIG. 3. The carbonlike A_1 mode of carbon-hydrogen complexes for samples doped with ^{12}C (dash-dot line) and the one doped with ^{12}C and ^{13}C (solid line).

In the spectral region close to the isolated carbon LVM, shown in Fig. 2, two other lines were observed in the IR absorption spectra. The first one, which for ^{12}C occurs at 518.2 cm^{-1}, with an isotopic separation of 15.4 cm^{-1}, was attributed to the transverse E^+ mode of the C-H complex in comparison with other carbon-doped III-Vs, such as InP and GaAs (see Table I).[10] The Raman scattering intensity of this mode is very low (Fig. 1) consistent with its weak Raman intensity in GaAs (Ref. 11) and InP.[4] We were not able to identify the other line located for ^{12}C at 508 cm^{-1} with isotopic separation of 12.8 cm^{-1}.

Figure 4 shows the high frequency range of the IR spectra measured at $T=25$ K for samples doped with pure ^{12}C and a mixture of ^{12}C and ^{13}C. The strongest mode for ^{12}C appears at 2686.5 cm^{-1} with an isotopic separation of 7.7 cm^{-1}. A similar line was attributed to the A_1^- stretch mode of the C-H complex observed in several other III-Vs such as InP, GaAs, and AlAs. There are two other weak modes for ^{12}C at

TABLE I. Summary of all detected LVMs for InAs:C and the corresponding values for InP:C and GaAs:C.

	LVM frequency (ν) cm^{-1}			Isotopic separation $\nu(^{12}\mathrm{C})-\nu(^{13}\mathrm{C})$		
Mode	InAs (20 K)	InP (10 K)	GaAs (10 K)	InAs	InP	GaAs
^{12}C	530	546.9[a]	582.8[c]	19	20.1	21
H-^{12}C(A_1^+)	393.2	413.5[a]	452.7[c]	13.5	ND	14.9
H-^{12}C (E^+)	518.2	521.1[a]	562.6[c]	15.4	ND	15
H-^{12}C (A_1^-) str	2686.5	2703.3[a]	2635.2[c]	7.7	6.7	6.7
H-^{12}C$_2$ str	2756.9	ND	2688[d]	5	ND	ND
H$_2$-^{12}C$_2$ str	2819.6	ND	2725[e]	8.6	ND	ND
^{12}C-^{12}C	1832	1814[b]	1856[f]			
^{13}C-^{12}C	1794		1824[f]			
^{13}C-^{13}C	1758		1788[f]			

[a] Reference 10.
[b] Reference 15.
[c] Reference 21.
[d] Reference 22.
[e] Reference 23.
[f] Reference 13.

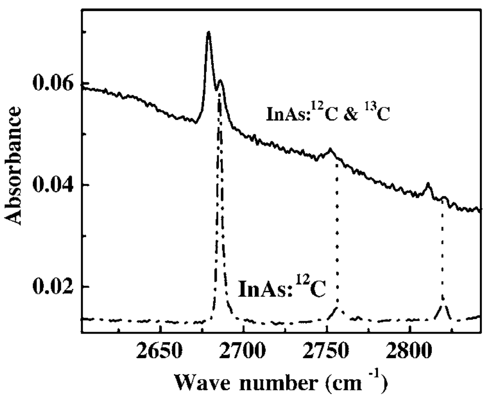

FIG. 4. Low temperature (T=20 K) IR spectra of InAs:^{12}C and InAs:^{12}C and ^{13}C in the high frequency range.

frequencies of 2756.9 and 2819.6 cm^{-1}with isotopic separations of 5 and 8.6 cm^{-1} respectively. These two lines can be assigned to other complexes of carbon-hydrogen such as H-C$_2$ and H$_2$-C$_2$ that are believed to be formed in highly doped GaAs samples.[12] A summary of all mode energies and their comparison with accepted modes in GaAs and InP is shown in Table I.

C. LVMs of dicarbon centers

Low temperature (T=20 K) Raman measurements were conducted on as grown and annealed InAs samples doped with pure ^{12}C and the mixture of ^{12}C and ^{13}C. Figure 5 demonstrates the spectra of both samples in the frequency range of 1500 to 2000 cm^{-1}. Three lines at frequencies of 1758, 1794, and 1832 cm^{-1} in the spectrum of the mixed isotope sample, were assigned to directly bonded dicarbon complexes. These mode energies are in the range of typical single C-C bond energies observed in organic compounds. The isotopic ratio of the ^{12}C-^{12}C frequency to that of ^{13}C-^{13}C is 1.042 compared to $(13/12)^{0.5}=1.041$. Considering that this sample is doped with %70 ^{13}C and %30 ^{12}C, the probability ratio of having ^{13}C-^{13}C, ^{13}C-^{12}C, and ^{12}C-^{12}C bonds is 5.4 : 4.7 : 1. The ratio of the area under the three peaks in the spectrum is 5.9 : 4.0 : 1, respectively. The closeness of these ratios confirms our conclusion about their identity.

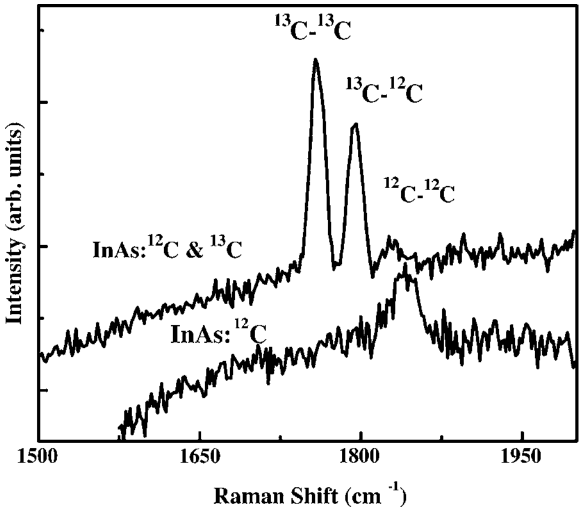

FIG. 5. Low temperature (T=25 K) Raman spectra of the samples doped with ^{12}C and ^{13}C showing the LVMs arising from dicarbon centers.

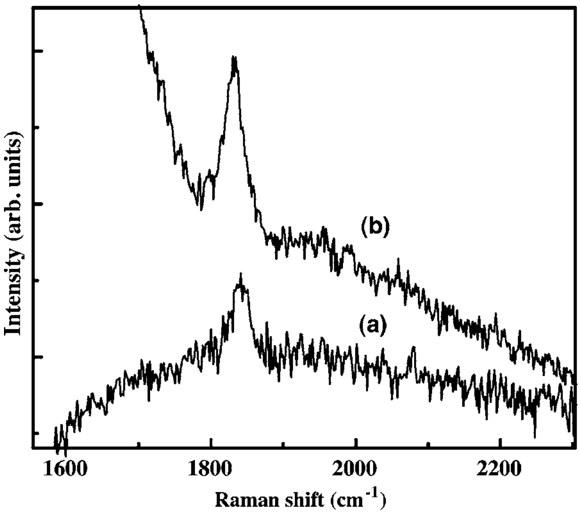

FIG. 6. Raman spectra of the as-grown (a) and annealed (b) sample doped with ^{12}C.

Figure 6 shows the Raman spectra for the sample doped with ^{12}C as grown (a) and after being annealed at 450 °C (b). The intensity of the C-C peak increased by a factor of 2 after annealing.

Two Raman LVMs in the frequency range of 1700 to 1900 cm^{-1} have been observed for other ^{12}C-doped III-Vs such as GaAs and AlAs after being annealed at temperatures higher than 600 °C,[13,14] and also in as-grown and annealed InP.[15] According to theoretical calculations,[14] these two peaks arise from two different orientations of the C-C defect aligned along (111) and (110) directions centered on the As lattice site. For InAs we only detected the higher frequency line for the as-grown samples. These modes are not observed in IR, in agreement with theoretical and experimental results in GaAs indicating that the induced dipole moments of the C-C stretch modes are almost zero and these modes are not IR active.[14]

IV. DISCUSSION

According to the mass defect model, the LVM frequency of two isotopes of the isolated carbon defect should satisfy the following relationship considering that the force constant-related parameters are the same for both isotopes:

$$\omega_{\mathrm{imp}}^2 = k\left[1/\chi M_{\mathrm{NN}} + 1/m_{\mathrm{imp}}\right].$$

In this relationship M_{NN} and m_{imp} are the masses of the nearest neighbor and impurity atoms, respectively, k is the force constant, and χ is a parameter related to bond bending and according to the theoretical calculations can vary in the range of 1.3 to 6.4.[16] This criterion was used to rule out the presence of carbon donors in InP.[12] Using this model for ^{13}C and ^{12}C LVMs and replacing M_{NN} with the mass of In and As, gives two values of 2.31 and 1.51, respectively, for χ that both are acceptable. Therefore this model could not be used to make a conclusion about the lattice site of the carbon atoms.

In Table I, we have summarized all the observed LVM frequencies for InAs:C along with those for GaAs:C and InP:C. The existence of five modes related to carbon-hydrogen complexes with frequencies that are very close to those of carbon acceptor-hydrogen pairs in other III-V semiconductors provides strong support for the conclusion that isolated carbon is an acceptor in InAs, and that it complexes with hydrogen in the same manner as the other III-V's. The observed C-H modes are consistent with hydrogen occupying a bond-center position. A donor-hydrogen complex usually forms by hydrogen locating adjacent to the donor atom along the anti-bonding orbital and it gives rise to two vibrational modes. For example in GaAs:$\mathrm{Si_{Ga}}$ two LVMs were detected at 896 and 1717 $\mathrm{cm^{-1}}$ which were assigned to transverse and longitudinal stretch modes of Si-H complex respectively.[17] This should be compared to the A_1^- mode energy of 2095.7 $\mathrm{cm^{-1}}$ for $\mathrm{Si_{As}}$-H.[18] We therefore conclude that the observed C-H modes are not consistent with the presence of substitutional carbon donors in InAs.

The possibility of assigning the unidentified modes at 508 and 495 $\mathrm{cm^{-1}}$ (Fig. 2) to ^{12}C and ^{13}C donors occupying In lattice site was ruled out using the mass defect model, since it gives the unacceptable value of 0.3 for χ. Given that we see no evidence of isolated carbon donors, we must look to the presence of more complex defects to explain the observed n-type properties of C-doped InAs. We believe that the dicarbon defects observed in this work using Raman scattering offer a plausible explanation. According to the theoretical calculations for GaAs:C,[19] this complex is a deep donor split interstitial defect and can be formed if some carbon atoms diffuse to interstitial sites and get trapped by substitutional carbon atoms. The fact that C-C centers can not be detected in GaAs and AlAs unless the samples are annealed at high temperatures, is due to the very low diffusion coefficient of carbon in these materials. On the other hand, the observation of C-C LVMs in as-grown InP (Ref. 15) and InAs is a sign of a higher diffusion coefficient of carbon in these compounds. This difference can be explained by the weaker bonding of carbon to In atoms compared to Ga or Al atoms[20] that makes the movement of carbon atoms to interstitial sites and consequently the formation of C-C defects, easier. In addition, the low temperature growth used in the preparation of these samples may result in the presence of high concentrations of native defects, which could result in the observed high diffusion effects.

V. CONCLUSIONS

In summary, carbon-doped InAs layers were studied by Raman and IR spectroscopy. Previously detected LVMs of isolated carbon atoms at 527 $\mathrm{cm^{-1}}$ were attributed to substitutional atoms occupying the As lattice sites. It was shown that carbon acceptors are passivated by hydrogen atoms located at the bond-center position between carbon and In atoms. These complexes give rise to five IR-active modes detected in this work. Substitutional C-C complexes were also detected by Raman spectroscopy and they were proposed to be responsible for the n-type conductivity of InAs:C.

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