Carbon acceptors and carbon-hydrogen complexes in AlSb

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Aluminum antimonide (AlSb) has potential applications as a radiation detector and as a material in high-mobility heterostructures. As-grown AlSb exhibits *p*-type conductivity. Using infrared absorption spectroscopy, we have observed local vibrational modes (LVM's) arising from carbon impurities in *n*- and *p*-type AlSb. The first and second harmonics of the ^{12}C mode have frequencies of 591.6 and 1179.2 cm^{-1}, respectively, at liquid-helium temperatures. A peak at 572.9 cm^{-1} is tentatively identified as the ^{13}C LVM. Carbon-hydrogen complexes were formed by annealing *p*-type AlSb in hydrogen gas, yielding a C-H stretch mode at 2566.6 cm^{-1}. Our results indicate that during the growth of bulk AlSb, carbon contamination may be an important source of unintentional *p*-type doping.

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Aluminum antimonide (AlSb), a compound semiconductor with an indirect band gap of 1.7 eV, has potential applications as a radiation detector,[1] due to its large band gap and the high atomic number of antimony.[2] AlSb also is used in high-mobility AlSb/InAs heterostructures.[3,4] Bulk AlSb grown by the Czochralski method commonly exhibits *p*-type conductivity.[5] Such unintentional doping is detrimental to the fabrication of devices with good carrier transport characteristics. Selenium-doped AlSb, for example, exhibits persistent optical absorption,[6] a property that has been used to write volume absorption holograms.[7] The presence of compensating acceptors, however, limits the doping level achieved in such *n*-type semiconductors. In this paper, we propose that carbon impurities are unintentionally introduced into bulk AlSb during growth, resulting in *p*-type conductivity. Substitutional carbon impurities give rise to a local vibrational mode (LVM) that is observed with Fourier-transform infrared (FTIR) spectroscopy.

A similar situation occurs in GaAs grown by the liquid-encapsulated Czochralski technique, in which carbon is an important residual contaminant in semi-insulating material.[8] The substitutional acceptors $^{12}C_{As}$ and $^{13}C_{As}$ give rise to LVM frequencies of 582 and 562 cm^{-1}, respectively.[9] When hydrogen is introduced into GaAs:C, neutral carbon-hydrogen complexes are formed, which have a stretch-mode frequency of 2635 cm^{-1} at liquid-helium temperatures.[9] In AlSb, Se-H, and Te-H complexes were formed by annealing in hydrogen gas at temperatures between 700 and 950 °C.[10] In this study, carbon-hydrogen complexes were formed by annealing *p*-type AlSb in hydrogen at a temperature of 900 °C.

AlSb:Se and AlSb:S crystals were grown by the Czochralski technique from antimony-enriched melts. In the case of AlSb:Se, the samples contain more selenium donors than carbon acceptors, so that they are *n*-type. For AlSb:S, the acceptor concentration exceeds that of the sulfur donors, so that they are *p*-type. Mid-infrared (IR) spectra were obtained with a Bomem DA8 vacuum FTIR spectrometer with a KBr beamsplitter, covering the range from 500 to 4000 cm^{-1}. The instrumental resolution was 1 cm^{-1}. Samples were placed in a Janis STVP-100 liquid-helium cryostat with ZnSe windows. Measurements taken at liquid-helium temperatures (8–10 K) utilized a Ge:Cu photoconductor detector[11] mounted directly behind the sample. Variable-temperature measurements utilized a mercury cadmium telluride (MCT) detector outside the cryostat. Room-temperature Hall effect measurements (MMR Technologies, Inc.) were performed in the van der Pauw geometry using indium contacts.

An IR absorption peak at approximately 592 cm^{-1} was observed in two samples, along with two-phonon absorption features, as shown in Fig. 1. The phonon absorption peaks were observed previously,[12] but the peak at 592 cm^{-1} was not. The frequency of the 592 cm^{-1} mode is similar to LVM frequencies arising from carbon acceptors in GaAs (582 cm^{-1}),[13] AlAs (631.5 cm^{-1}),[14,15] GaP (606 cm^{-1}),[16] and InP (547 cm^{-1}).[17] Hence, we ascribe the mode at 592 cm^{-1} to carbon acceptors in AlSb. The frequency of the mode in

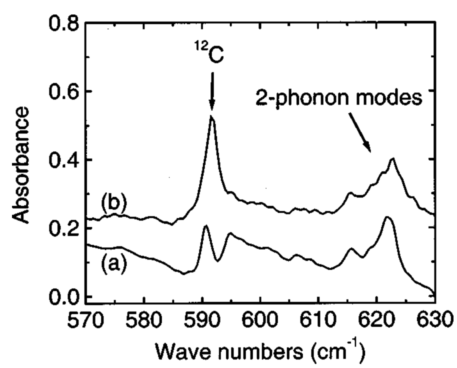

FIG. 1. IR absorption spectra of (a) *p*-type AlSb:S and (b) *n*-type AlSb:Se, at liquid-helium temperatures. The ^{12}C LVM peak and two-phonon modes are indicated.

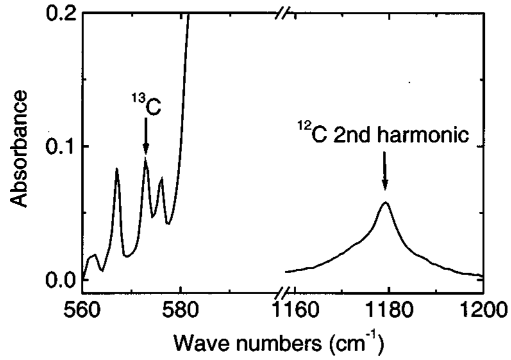

FIG. 2. IR absorption spectrum of thick (3-mm) AlSb:Se. A peak identified as the ^{13}C LVM is indicated. The second harmonic of the ^{12}C LVM is also observed.

AlSb:S and AlSb:Se is 590.7 and 591.6 cm^{-1}, respectively. The two-phonon peak at 622 cm^{-1} is approximately 1 cm^{-1} higher in AlSb:Se than in AlSb:S. The slightly higher frequencies in the AlSb:Se sample may result from compressive strain, due to the high concentration of carbon and selenium doping. The larger linewidth of the carbon LVM in AlSb:Se (2.5 cm^{-1}) as compared to AlSb:S (1.7 cm^{-1}) is consistent with the presence of inhomogeneous strain.

Secondary-ion mass spectrometry (SIMS) measurements were performed on samples taken from the same ingot as the AlSb:Se sample, and yielded concentrations of $[\mathrm{Se}]=4\times10^{18}\,\mathrm{cm}^{-3}$ and $[\mathrm{C}]=7\times10^{17}\,\mathrm{cm}^{-3}$. The integrated absorbance (IA) is defined as

$$\mathrm{IA}=\int \alpha(\nu)d\nu,$$

where $\alpha(\nu)$ is the absorption coefficient (cm^{-1}) and ν is the LVM frequency in wave numbers (cm^{-1}). The IA for the ^{12}C LVM in AlSb:Se is 110 cm^{-2}. SIMS measurements were not performed on the AlSb:S sample. However, Hall effect measurements showed a free-hole concentration of $1.2\times10^{17}\,\mathrm{cm}^{-3}$. If the holes originate from carbon acceptors, then an uncompensated sample would yield an IA of 19 cm^{-2}, based on the AlSb:Se results. The measured value of the IA in AlSb:S is 26 cm^{-2}, consistent with the hypothesis that carbon acceptors are partially compensated by sulfur donors. By way of comparison, in GaAs, a carbon concentration of $7\times10^{17}\,\mathrm{cm}^{-3}$ would yield $\mathrm{IA}=65\pm10\,\mathrm{cm}^{-2}$, a value that is reasonably close to the IA measured for the AlSb:Se sample.[8]

An IR absorption spectrum from a thick (3-mm) AlSb:Se sample is shown in Fig. 2. Due to the thickness of this sample, the spectral region near the 592-cm^{-1} mode is opaque. On the low-energy side of the 592-cm^{-1} mode, several peaks are observed. We tentatively identify the peak at 572.9 cm^{-1} as the LVM arising from ^{13}C impurities. The ratio of intensities is IA(^{13}C)/IA(^{12}C)$=0.01$, in agreement with the natural abundance of carbon isotopes. The isotopic frequency shift is $\nu(^{12}\mathrm{C})/\nu(^{13}\mathrm{C})=1.0326$. By way of comparison, the ^{12}C and ^{13}C LVM frequencies in AlAs are 631.5 and 608.5 cm^{-1}, respectively, for an isotopic frequency shift of $\nu(^{12}\mathrm{C})/\nu(^{13}\mathrm{C})=1.0378$. The identities of the other peaks are not known. It is possible that they are due to selenium-related complexes. Thick AlSb:S samples could not be investigated in this frequency range due to free carrier absorption.

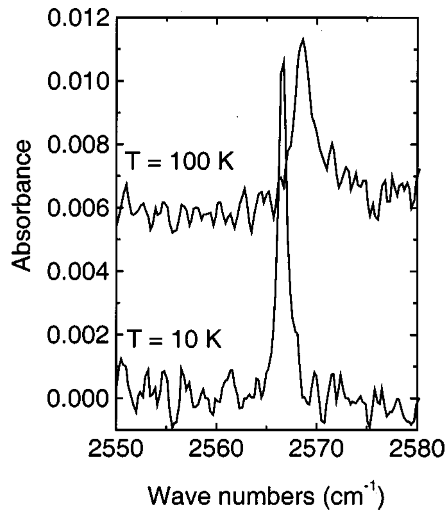

FIG. 3. IR absorption spectrum of AlSb:C,H, at a temperature of 10 and 100 K. The peak corresponds to the C-H stretch mode.

To test the validity of our assignment for the ^{13}C mode, a three-dimensional numerical simulation was performed, using a 64-atom molecule, with an adjustable force constant between neighboring atoms. In this simple spring-and-mass

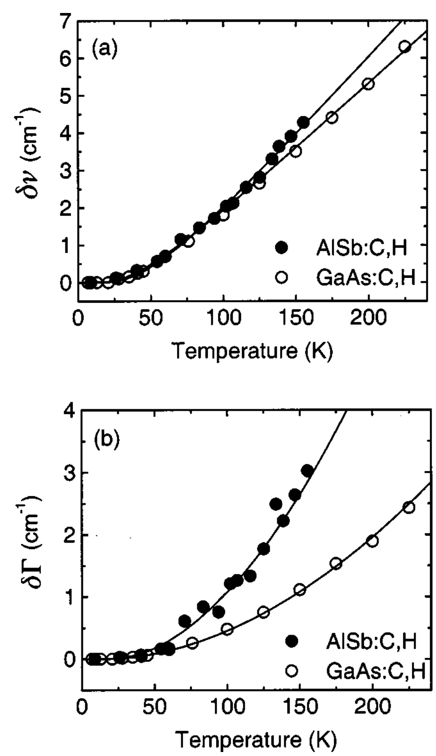

FIG. 4. Temperature-dependent shifts in (a) frequency and (b) linewidth, of C-H stretch modes in AlSb (this work) and GaAs (Ref. 20).

TABLE I. Carbon and carbon-hydrogen LVM frequencies in III–V semiconductors.

Material	$\nu(^{12}\mathrm{C})$ (cm^{-1})	$\nu(^{13}\mathrm{C})$ (cm^{-1})	$\nu(^{12}\mathrm{C})/\nu(^{13}\mathrm{C})$	$\nu(^{12}\mathrm{C\text{-}H})$ (cm^{-1})	$\nu(^{12}\mathrm{C\text{-}D})$ (cm^{-1})	$\nu(^{12}\mathrm{C\text{-}H})/\nu(^{12}\mathrm{C\text{-}D})$
AlAs[a]	631.5	608.5	1.0378	2558.1	1902.6	1.3445
AlSb[b]	591.6	572.9	1.0326	2566.6	ND	—
GaAs[c]	582.8	561.8	1.0374	2635.2	1968.6	1.3389
GaP[d]	606	ND[f]	—	2660.2	1980.8	1.3430
InP[e]	546.9	526.8	1.0382	2703.3	ND	—

[a]Pritchard *et al.* (Ref. 15).
[b]This work. ^{12}C and ^{13}C modes are for the AlSb:Se sample, whereas the ^{12}C-H mode is for the AlSb:S sample.
[c]Davidson *et al.* (Ref. 9).
[d]Hayes *et al.* (Ref. 16) and Clerjaud *et al.* (Ref. 23).
[e]Davidson *et al.* (Ref. 17).
[f]ND not discovered.

model, bending force constants and anharmonic effects were neglected. The Al-Sb force constant was adjusted so that the maximum vibrational frequency matched the TO-phonon frequency of AlSb (320 cm^{-1}). One ^{122}Sb atom was replaced by a ^{12}C atom, and the Al-C force constant was adjusted to yield the observed LVM frequency of 591.6 cm^{-1}. The ^{12}C atom was then replaced by a ^{13}C atom. The mass substitution yielded an LVM frequency of 574.9 cm^{-1}, in good agreement with our experimental value of 572.9 cm^{-1}. However, the peak at 575.9 cm^{-1} (Fig. 2) must also be considered as a candidate for the ^{13}C mode.

In the thick AlSb:Se sample, an IR absorption peak at 1179.2 cm^{-1} was observed. Since this frequency is nearly twice that of the 592-cm^{-1} mode, this peak is ascribed to the second harmonic of the carbon LVM. The ratio of the second-harmonic to fundamental frequencies is 1179.2/591.6 = 1.993. The intensity of the second harmonic is 1.7% that of the fundamental transition. In GaAs, the carbon fundamental and second-harmonic modes exhibit fine structure due to the different configurations of nearest-neighbor gallium isotopes.[18,19] In AlSb, the carbon nearest neighbors are aluminum atoms, which only have one stable isotope (27 amu), so that no fine structure is observed.

To further investigate carbon doping in AlSb, carbon-hydrogen complexes were formed. A *p*-type AlSb sample was annealed in a quartz ampoule filled with $\frac{2}{3}$ atm of hydrogen for 1 h at a temperature of 900 °C. After the hydrogen diffusion, the sample was rapidly quenched to room temperature by dropping the ampoule into ethylene glycol. In the hydrogenated sample, a new IR absorption peak appeared at 2566.6 cm^{-1} (Fig. 3). The frequency of the peak is similar to those of C-H stretch modes in other III–V semiconductors (Table I). Hence, the peak at 2566.6 cm^{-1} is attributed to a ^{12}O-H stretch mode. The fact that carbon-hydrogen complexes form in *p*-type samples, and not *n*-type samples, supports our claim that the carbon impurities are acceptors. If they were donors, then they would be passivated in *n*-type AlSb:Se (Ref. 10) but not in *p*-type AlSb:S.

As the sample temperature is increased, the peak frequency increases slightly. The LVM frequency and width are plotted as a function of temperature in Fig. 4 for C-H complexes in AlSb. As a comparison, the corresponding values for C–H complexes in GaAs were plotted. The temperature dependence for hydrogen LVM's in GaAs is well described by a model in which the complex interacts with a single acoustical phonon.[20] In the weak-coupling limit, this interaction leads to a temperature-dependent frequency shift given by

$$\delta\nu = \frac{\delta\nu_0}{e^{h\nu_0/kT}-1}$$

and linewidth broadening given by

$$\delta\Gamma = \frac{2(\delta\nu_0)^2}{\eta}\frac{e^{h\nu_0/kT}}{(e^{h\nu_0/kT}-1)^2},$$

where $\delta\theta_0$, ν_0, and η are adjustable parameters, k is Boltzmann's constant, and T is temperature.

For the AlSb:C,H complex, a fit to the data yields $\delta\nu_0 = 6\ \mathrm{cm}^{-1}$, $\nu_0 = 96\ \mathrm{cm}^{-1}$, and $\eta = 30\ \mathrm{cm}^{-1}$. From these parameters, one can calculate a zero-temperature, homogeneous linewidth of 0.6 cm^{-1}.[21] However, the linewidth that we measured at low temperatures was equal to the instrumental broadening (1 cm^{-1}), so that this calculated linewidth could not be verified. For GaAs:C,H, the values are $\delta\nu_0 = 4\ \mathrm{cm}^{-1}$, $\nu_0 = 78\ \mathrm{cm}^{-1}$, and $\eta = 51\ \mathrm{cm}^{-1}$. As seen in Fig. 4, the frequency shifts in AlSb and GaAs are nearly identical. However, the temperature-dependent broadening is greater in the case of AlSb. It is interesting to note that the LVM frequency of C-H complexes increases with increasing temperature, in contrast to most other hydrogen-related complexes, in which the frequencies decrease with temperature.[22] The reason for this difference is not known.

In conclusion, using IR spectroscopy, Hall effect, and SIMS measurements, we have presented evidence that carbon impurities are acceptors in AlSb. LVM's arising from carbon impurities and carbon-hydrogen complexes have been identified. During the growth of bulk AlSb, carbon contamination may be an important source of unintentional *p*-type doping.

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