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Heavily carbon-doped GaAsSb grown on InP for HBT applications

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Abstract

We present the results of Hall measurements on heavily carbon-doped GaAsSb epilayers grown by metalorganic chemical vapour deposition (MOVPE) on InP substrates. An extremely strong alloy scattering effect is observed in this material, dominating the Hall mobility even at doping levels in the 10^{19} range. This effect is due to the very large (1 eV) valence band offset between GaAs and GaSb. Despite the strong alloy scattering, conductivities as high as 890 S/cm were observed at doping levels above 10^{20} cm^{-3} . CCl_4 and CBr_4 were investigated as p-type dopants. Hole concentrations of up to 1.4×10^{20} and $3.0 \times 10^{20} \text{ cm}^{-3}$ were obtained at growth temperatures of 560°C and 500°C, respectively. For both carbon sources, a strong reduction in growth rate and Sb incorporation rate was observed with increasing dopant concentration at 560°C. Carbon incorporation was observed to increase linearly with Sb solid phase mole fraction. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Heavy p-type carbon doping of GaAs has been demonstrated by metalorganic vapour-phase epitaxy (MOVPE) using a variety of precursors including trimethylarsenic [1], CCl_4 [2], and CBr_4 [3]. Doping levels well above 10^{20} cm^{-3} have

been demonstrated, and high-speed GaAs-based heterojunction bipolar transistors (HBTs) utilising a heavily carbon-doped base are now in commercial production. In an attempt to achieve higher oscillation frequencies and lower operating voltages than are possible with GaAs, our group has investigated the use of p-type GaAsSb layers as the base region in InP/GaAsSb/InP double heterojunction bipolar transistors (DHBTs) [4,5]. This has permitted cut-off frequencies in excess of 150 GHz [6]. There has been very little previous work on the study of the incorporation of carbon in GaAsSb alloys. Bhat et al. [7], McDermott et al. [8] and Xu et al. [4] reported the use of CCl_4 to

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achieve doping levels of up to $1 \times 10^{20} \text{ cm}^{-3}$. CBr_4 has been reported to result in excellent doping characteristics in GaAs, however its use in GaAsSb has not been reported. An unexplained aspect of previous work is the fact that the observed drift mobilities are significantly lower than those of InGaAs at comparable carrier concentrations, despite the fact the effective hole masses of the two alloys are comparable. Since the maximum oscillation frequency f_{max} is proportional to $1/\sqrt{R_B}$ where R_B is the base sheet resistance, it is therefore of considerable importance to investigate the cause of this lower mobility, and the implications for HBTs.

In this work, we study several aspects of p-type transport and dopant incorporation in this material. We demonstrate that the room temperature mobility is strongly limited by alloy scattering even up to the 10^{19} – 10^{20} cm^{-3} doping range. We present the results of fitting to a simple alloy scattering model, which accounts for the observed drop in mobility in this material compared with InGaAs. Hall carrier concentrations of up to $3.0 \times 10^{20} \text{ cm}^{-3}$ and conductivities of up to 890 S/cm have been achieved. Two different carbon precursors, CCl_4 and CBr_4 have been investigated and both show a strong effect on the growth rate and alloy composition at 560°C for extremely high doping levels.

2. Experimental procedure

All samples were grown by MOVPE in a conventional quartz horizontal reactor chamber operating at 100 Torr with a total H_2 carrier flow of 6 standard litres per minute. Growth temperatures were between 500°C and 560°C . GaAsSb growth was achieved using triethylgallium (TEGa, 18°C), tertiarybutylarsine (TBAs, -15°C), and trimethylantimony (TMSb, -15°C). Liquid CBr_4 (18°C) and a gaseous mixture of 500 ppm CCl_4 in hydrogen were used as the carbon sources. A thin ~ 3 monolayer cap of InP was deposited as a cap layer to protect the surface during cool-down under TBP. It was found that direct cooling of the GaAsSb surface under TBAs/TMSb resulted in the formation of very fine pits observable by atomic force micro-

scope [4]. Growth rates were in the range 1 – 3 \AA/s , and were determined by high-resolution (004) X-ray diffraction scans, based on the observation of interference fringes due to mismatch between the InP and the GaAsSb epilayers. Alloy samples were grown primarily on Fe-doped InP epilayers using trimethylindium (TMIn) and tertiarybutylphosphine (TBP). Hall measurements were performed at 294 K using the van der Pauw geometry at a magnetic field of 5000 G . Epilayer thicknesses were in the range 500 – 1200 \AA . In–Zn metal contacts were formed under a flowing hydrogen ambient at 300 – 350°C . Hall measurements were performed on as-grown samples with no additional annealing.

3. Results and discussion

Previous reports of the Hall mobilities of heavily doped GaAsSb samples, nominally lattice matched to InP, were in the range of 30 – $40 \text{ cm}^2/\text{Vs}$ [7,8]. The exact Sb mole fractions were not stated in those works. Hall data for a series of layers grown in this study in the entire composition range from $x = 0$ to 1 are summarised in Fig. 1 below. All samples for this figure had measured Hall concentrations in the range from 1×10^{19} to $1 \times 10^{20} \text{ cm}^{-3}$. The data show a strong reduction in mobility values for the alloy samples compared with the binary endpoints. This reduction is not associated with source impurities: a binary GaAs layer grown on a GaAs substrate showed a room temperature mobility of $74 \text{ cm}^2/\text{Vs}$ at a carrier concentration of $2.2 \times 10^{19} \text{ cm}^{-3}$, within the range of previous reports. GaSb binary layers grown on GaAs substrates showed mobilities as high as $150 \text{ cm}^2/\text{Vs}$ at a doping level of $1.6 \times 10^{19} \text{ cm}^{-3}$ despite the presence of dislocation densities of at least 10^{12} cm^{-2} . For intermediate compositions, a slight tendency towards somewhat higher mobility values on the Sb-rich side is evident. The suppression of hole mobility for the alloy is qualitatively similar to that observed in p-type AlGaAs in which a similar dip is observed, albeit at substantially lower doping levels (10^{17} range) [9]. Alloy scattering is the most likely explanation for this behaviour and was already proposed by Cherng et al. [10] to explain the temperature

dependence of the hole mobility in undoped GaAsSb. In contrast to other III–V materials, alloy scattering apparently dominates the mobility of GaAsSb even at high p-type doping levels of 10^{19} cm^{-3} or greater. Ito et al. have investigated heavily C-doped InGaAs over the entire composition range and do not observe a dip of the kind reported here [11]. Given that the valence band offset between coherently strained GaAs and GaSb is estimated [12] to be around 1 eV, compared with 440 meV for InAs and GaAs [13], the difference between these two alloys is not surprising. We have employed a simple pseudobinary model due to Harrison and Hausser [14], in which holes in a uniform alloy experience scattering from a random potential of atomic dimensions. The strength of this potential V_{AB} is taken as an adjustable parameter. The exact physical significance of V_{AB} has been the subject of much discussion, however, we favour the interpretation that it is related to the valence band offset between GaAs and GaSb, which is considerably larger for this material system than most III–V s. The dotted line in Fig. 1 shows the expected behaviour for ionized impurity scattering, in which the mobility μ_{II} is proportional to $m_h^{-1/2}$. We obtained the fit to the experimental data by expressing the total mobility as

$$\frac{1}{\mu} = \frac{1}{\mu_{\text{alloy}}} + \frac{1}{\mu_{II}}.$$

The best fit is obtained with a scattering potential $V_{AB} = 2.5 \text{ eV}$. This is considerably larger than the estimated band offset between GaAs and GaSb, however the model is highly simplified and depends strongly on the length scale of the alloy fluctuations, which for the mobility expression used here was assumed to be the nearest-neighbour separation.

Fig. 2 shows the dependence of the Hall mobility on carrier concentration for a number of samples grown at various temperatures, V:III ratios, and Sb mole fractions. Different symbols are used to represent ranges of the Sb mole fraction in the solid phase. The dependence on doping level is weak, as expected given the strong effect of alloy scattering. There is a slight trend to higher mobility values for the higher Sb compositions, however there is much

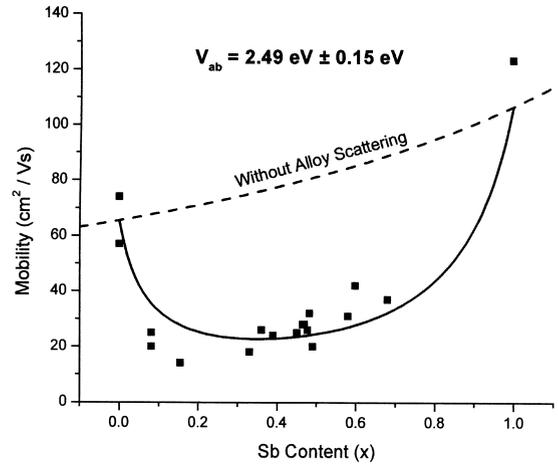


Fig. 1. Hall mobility as a function of x in $\text{GaAs}_{1-x}\text{Sb}_x$ epilayers. All layers had doping levels between 1×10^{19} and $1 \times 10^{20} \text{ cm}^{-3}$.

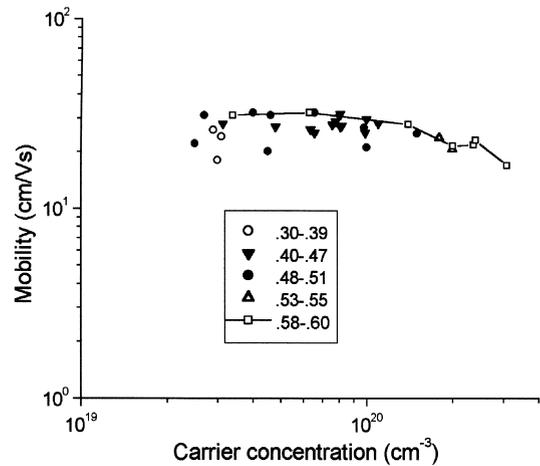


Fig. 2. Hall mobility as a function of carrier concentration. Different symbols correspond to the indicated Sb composition ranges.

sample-to-sample variation, the origin of which is unclear at present. The maximum mobility drops off by roughly 30% from the lowest doping level to the highest.

In Fig. 3, we show a plot of conductivity as a function of carrier concentration obtained for the same samples. Different symbols correspond to different Sb mole fraction ranges. All of the data fall on the same overall linear trend, with evidence of

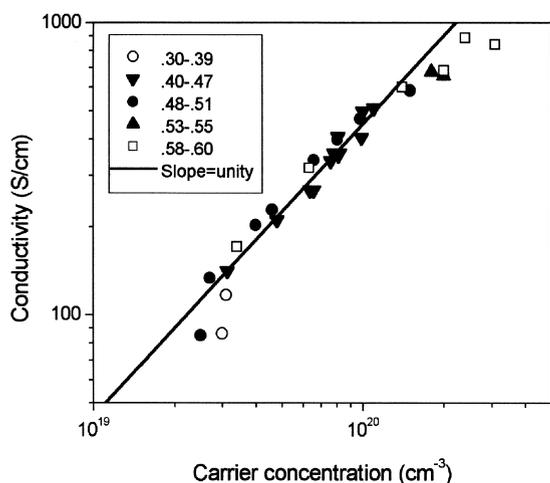


Fig. 3. Conductivity as a function of carrier concentration. Different symbols correspond to the indicated Sb composition ranges.

saturation above 10^{20} cm^{-3} . The maximum conductivity of 890 S/cm is observed at a doping level of around 2.5×10^{20} and is close to the value observed by Yamada et al. [15] of $\sim 1100 \text{ S/cm}$ in GaAs at this doping level. It should be noted that we could only achieve the highest carrier concentrations ($> 10^{20} \text{ cm}^{-3}$) on the Sb rich side. The fact that the conductivity closely follows a linear dependence on carrier concentration reflects the very weak dependence of the mobility on impurity concentration due to alloy scattering. Thus, with respect to majority carriers, there is no significant penalty in using the highest possible doping density in order to minimise base sheet resistance in HBTs.

It is well known that high flows of CCl_4 reduce the growth rate in MOVPE of GaAs due to etching by chloride radicals [2]. We observe a similar effect in GaAsSb, as documented in Fig. 4 for growth at 560°C and a V:III ratio of 2:1. The strong reduction in growth rate with increasing CCl_4 flows is matched by a corresponding reduction in Sb incorporation. These effects were observed to be greatly reduced at 500°C ; details will be reported elsewhere. Chloride etching and preferential In etching have also been well documented for InGaAs growth [16] using CCl_4 and have been attributed to the weaker In bond strength compared with Ga. A similar argument accounts for the observed

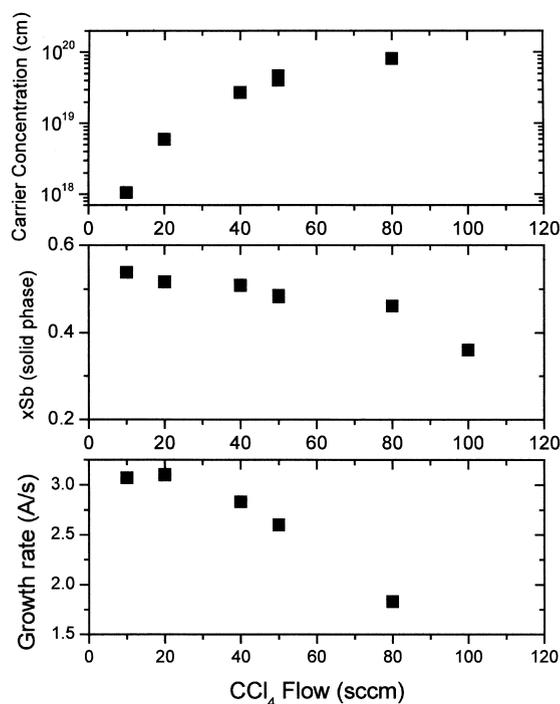


Fig. 4. Doping trends with CCl_4 at 560°C , V:III = 2:1.

reduction in the Sb mole fraction with increased doping in our GaAsSb samples. At 560°C , the doping level reaches a maximum of around $1 \times 10^{20} \text{ cm}^{-3}$ at a V:III ratio of 2.0. At lower growth temperatures, as discussed below, carbon doping levels of up to $2.5 \times 10^{20} \text{ cm}^{-3}$ were observed.

Fig. 5 shows the effect of varying the Sb mole fraction for two different growth temperatures. These data were obtained at a fixed CCl_4 flow of 75 sccm for the 500°C samples, and 100 sccm for the 560°C samples. Samples were grown at a fixed total V:III ratio of 2.4:1. Somewhat lower carrier concentrations were observed for the 560°C samples despite the fact that the CCl_4 flow was 33% higher. This is consistent with previous reports of CCl_4 doping in GaAs. For both temperatures we observed a roughly linear increase in carbon incorporation with increasing Sb mole fraction. This behaviour is exactly the opposite of the trend reported for InGaAs, where C acceptor incorporation becomes increasingly difficult at higher

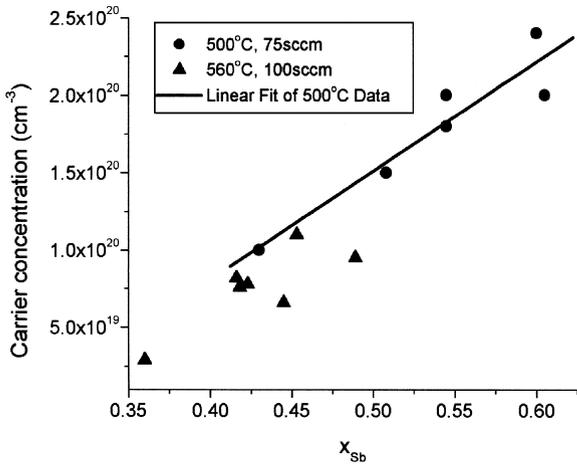


Fig. 5. Carbon and Sb incorporation trends with CCl_4 at 500°C and 560°C. The V:III ratio and CCl_4 flow were held constant at 2.4 while the Sb gas phase mole fraction was varied.

In content, requiring the use of very low growth temperatures or V:III ratios. This is due to the fact that carbon prefers to occupy the group III sublattice and is therefore a donor in InAs. In contrast, carbon is an effective p-type dopant in GaSb, where it occupies the group V sublattice. The GaSb sample shown in Fig. 1 had a p-type carrier concentration of $2.8 \times 10^{19} \text{ cm}^{-3}$. To our knowledge,

carbon doping of GaSb by MOVPE has not previously been reported. The trend of increasing C with increasing Sb content in GaAsSb is potentially very important for HBT applications, and offers a significant advantage over InGaAs, where doping levels over 10^{19} become increasingly more difficult to obtain at the compositions of technological interest. The increase in C-incorporation with Sb mole fraction is consistent with a strain energy argument in which the solubility of the acceptor is elevated over the zero strain limit because of the large mismatch in atomic radius between Sb and C.

Fig. 6 shows a summary of the influence of V:III ratio using CCl_4 . The Sb incorporation shows a clear increasing trend for decreasing V:III ratio. This is a thermodynamic effect due to the higher vapour pressure of As on the growth surface compared with Sb. The carbon incorporation also increases with decreasing V:III ratio as is observed in C-doping of GaAs. Two mechanisms can be postulated to explain this behaviour: (1) C and As/Sb compete for the same lattice sites and (2) strain energy considerations tend to favour the incorporation of C under Sb rich conditions (low V:III ratio) while suppressing it under As-rich conditions as illustrated by the data in Fig. 5. Further work is needed to distinguish between these two possibilities however, it is striking that the carbon and Sb

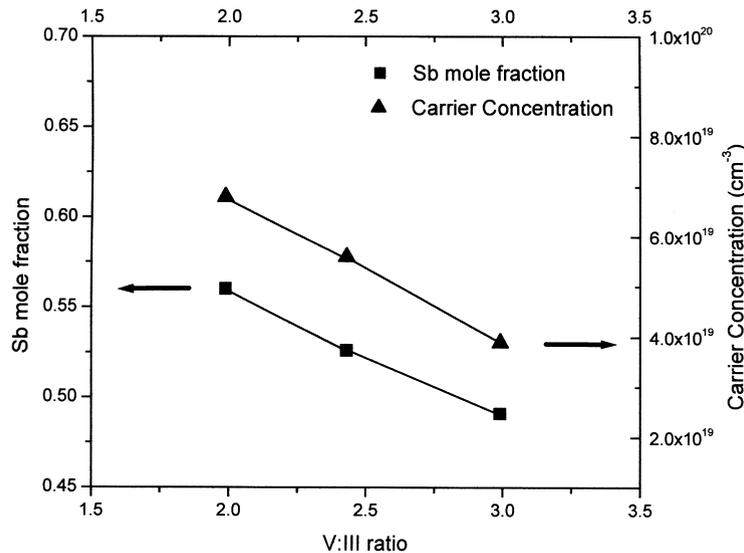


Fig. 6. Carbon and Sb incorporation trends as a function of V:III ratio at 560°C at a fixed CCl_4 flow of 50 sccm.

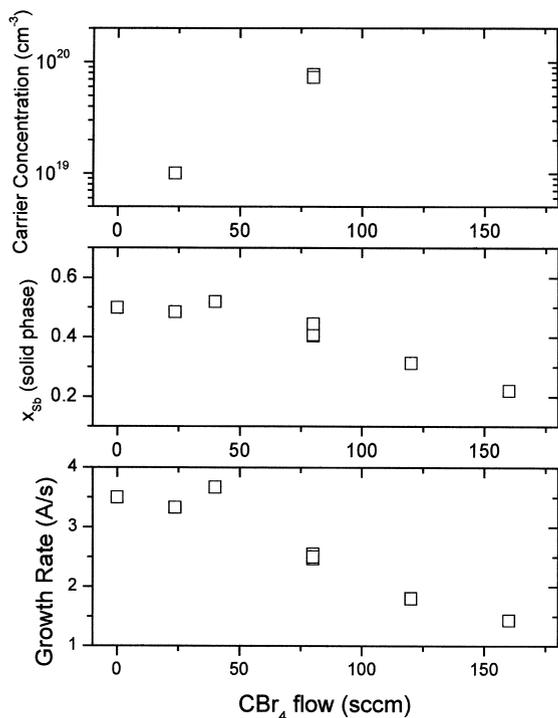


Fig. 7. Doping trends with CBr₄ at 560°C for a fixed V:III ratio of 2.4:1.

trends are so closely correlated, and this provides strong evidence for the role of strain.

CBr₄ has been extensively investigated as a carbon source for GaAs and InGaAs. We investigated its use here in an attempt to improve the mobility of the epilayers and perhaps reduce the etching effect of the dopant, however neither improvement was observed. Fig. 7 shows that both the growth rate and Sb incorporation are strongly affected by the CBr₄ flow, and that the trend is at least as strong as it was for CCl₄ doping. A maximum carrier concentration of 8×10^{19} was obtained at 560°C, which is directly comparable to CCl₄ under these conditions. At higher CBr₄ flows, the samples became too thin to achieve reliable Hall data. The doping efficiencies of CCl₄ and CBr₄ were observed to be comparable. For example, at 560°C doping levels of $\sim 8 \times 10^{19} \text{ cm}^{-3}$ were obtained using CCl₄ and CBr₄ flows of 2.3×10^{-6} and 1.5×10^{-6} mol/min, respectively.

4. Conclusions

We have presented a study of the transport properties of heavily C-doped GaAsSb. The Hall mobility is suppressed in comparison with InGaAs at comparable doping levels due to an anomalously large alloy scattering effect. Nevertheless, very high conductivity material can be obtained at doping levels of up to $3.0 \times 10^{20} \text{ cm}^{-3}$. CCl₄ and CBr₄ were both investigated as carbon dopants, and both show comparable strong interactions between doping level, growth rate and Sb mole fraction at very high doping levels. Finally, high doping levels can be achieved in this material without the use of annealing steps, or impractical low growth temperatures, in contrast to MOVPE-grown InGaAs.

Acknowledgements

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