Characterization of heavily carbon-doped GaAs grown by metalorganic chemical vapor deposition and metalorganic molecular beam epitaxy

Center for Compound Semiconductor Microelectronics, Materials Research Laboratory and Coordinated Science Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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Carbon-doped GaAs with carbon concentrations ranging from $2 \times 10^{17}$ cm$^{-3}$ to $2.6 \times 10^{20}$ cm$^{-3}$ has been characterized by variable temperature Hall effect measurements, secondary ion mass spectrometry (SIMS), and double-crystal x-ray diffraction (DCXD). The samples studied were grown by metalorganic chemical vapor deposition (MOCVD) and by metalorganic molecular beam epitaxy (MOMBE). The hole mobility is dominated by degenerate conduction for hole concentrations $>1 \times 10^{19}$ cm$^{-3}$, and the $77$ K resistivity is typically $30\%$-$35\%$ lower than at $300$ K in these samples. The mobilities of C-doped $p^+_z$-GaAs are found to be significantly higher than for Zn- or Be-doped $p^+_z$-GaAs for doping concentrations in excess of $2 \times 10^{18}$ cm$^{-3}$. The maximum achievable hole mobilities for C-doped material grown by the two techniques are nearly identical, indicating that neither MOCVD nor MOMBE has an inherent advantage over the other for producing low-resistivity $p$-type GaAs. SIMS analysis and Hall effect measurements reveal that the total carbon concentration, $[C]$, is higher than the as-grown hole concentration, $p_h$, in the most heavily doped samples. DCXD measurements show general agreement with the lattice mismatch predicted by Vegard's law. However, for $[C] > 10^{20}$ cm$^{-3}$ a discrepancy between the predicted and measured mismatch suggests that partial lattice relaxation or the presence of interstitial carbon may need to be considered in order to adequately describe the lattice contraction.

INTRODUCTION

Heavily doped $p$-type GaAs is of interest mainly due to its application in the base region of GaAs/AlGaAs $n$-$p$-$n$ heterojunction bipolar transistors (HBTs). The base region is made thin ($< 1000$ Å) to keep the base transit time small, so heavy doping ($p > 10^{19}$ cm$^{-3}$) is required to keep the external base resistance low. The cutoff frequency for unity current gain, $f_T$, is often limited in part by the base transit time, while the maximum frequency of oscillation for unity power gain, $f_{max}$, is typically limited by the $R_eC_e$ time constant, where $R_e$ is the external base resistance and $C_e$ is the base-collector junction capacitance. Thus, the ability to grow thin $p$-type layers of very low resistivity is important to the HBT process, and is critical in determining the high-frequency performance of such devices. Other considerations for the base region include the minority carrier transport across the base and control over the location and abruptness of the emitter-base junction.

The most common $p$-type dopants for GaAs-based device structures grown by metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) are Zn and Be, respectively. The memory effect associated with the Zn precursors in MOCVD is often minimized by employing a pause between growth of the base and emitter, while thin ($\approx 100$ Å) undoped GaAs spacer layers are often used to accommodate small amounts of base dopant diffusion. Displacement of the emitter-base junction into the wide gap emitter (typically $Al_xGa_{1-x}As$, $x \approx 0.3$) due to diffusion of the base dopant during growth or subsequent thermal processing can reduce the emitter injection efficiency. Several studies have shown that when the base doping exceeds $10^{19}$ cm$^{-3}$ for Be-doped GaAs grown by MBE and Zn-doped GaAs grown by MOCVD, significant diffusion of the base dopant into the emitter can occur. This effect is usually explained in terms of a substitutional-Interstitial diffusion mechanism for both Be and Zn at high concentrations.

Carbon has recently become a commonly used acceptor species in GaAs/AlGaAs electrical and optical devices due to its low diffusion coefficient and the fact that high concentrations and abrupt doping profiles may be obtained. The diffusion coefficient of carbon in GaAs at concentrations of $5 \times 10^{18}$ cm$^{-3}$ has been measured to be much lower than that for Be or Zn. Recently, very high C concentrations ($> 10^{20}$ cm$^{-3}$) have been obtained in GaAs using trimethylgallium (TMGa) as a dopant source in metalorganic molecular beam epitaxy (MOMBE) and CCl$_4$ as a source in MOCVD. Thin layers of such material are expected to provide the advantages of low resistivity and abrupt doping profiles. Detailed knowledge of the properties of such layers is essential for device modeling and also for gaining an understanding of any practical limitations that may be associated with the use of carbon in heavily doped layers.

In this article, we report the results of a study of the variation of the hole mobility of as-grown C-doped GaAs...
as a function of temperature, hole concentration, and total carbon concentration. The samples studied were grown by low-pressure metalorganic chemical vapor deposition (LP-MOCVD) with hole concentrations ranging from $10^{17}$ to $1.5 \times 10^{20}$ cm$^{-3}$, and by MOMBE with hole concentrations between $6 \times 10^{19}$ and $1.5 \times 10^{20}$ cm$^{-3}$. Variable-temperature Hall effect studies were carried out to investigate the electrical properties of these layers, and to make direct comparisons between the two growth techniques. Comparisons with Be-doped samples grown by gas source molecular beam epitaxy (GSMBE) and with results from Be- and Zn-doped GaAs reported in the literature are also made. For the samples studied here, secondary ion mass spectrometry (SIMS) has been used to determine the total carbon concentration, and double crystal x-ray diffraction (DCXD) and transmission electron microscopy (TEM) have been employed to study their structural properties.

**EXPERIMENT**

The MOCVD samples were grown in an Emcore GS3100 vertical low-pressure reactor. The growth precursors were TMGa and 100% AsH$_3$, and 2000 ppm CCl$_4$ in H$_2$ was used as the C dopant source. The growth pressure was maintained at either 76 or 100 Torr, and the substrate temperature was varied between 550 and 600°C. All growths were done on semi-insulating GaAs (100) substrates misoriented 2° towards (110). For samples with hole concentrations between $10^{17}$ cm$^{-3}$ and $1.5 \times 10^{19}$ cm$^{-3}$, the growth rate was 500 Å/min and the $V/III$ ratio was fixed at 65. The carbon concentration was controlled by varying the CCl$_4$ flow rate and the substrate temperature. Layer thicknesses were $\pm 0.5$ µm for most of the highly doped samples, and $\pm 2.5$ µm for the lightly doped ($p \approx 10^{17}$ cm$^{-3}$) samples, as determined by scanning electron microscope (SEM) measurements. The surface morphology was specular for most of the samples, but exhibited higher concentrations of defects in samples grown with high $V/III$ ratios and doped near $10^{19}$ cm$^{-3}$. $V/III$ ratios below 40 were necessary to achieve hole concentrations above $1.5 \times 10^{19}$ cm$^{-3}$. CCl$_4$-doped GaAs grown with extremely low $V/III$ ratios had better surface morphology than undoped GaAs grown under these conditions, and the growth rates were found to be as much as 30% lower than for undoped GaAs.

The C-doped MOMBE samples were grown in an MBE system modified for gas injection, using TMGa and solid As as sources. The TMGa serves as the source of Ga and C for the MOMBE-grown layers, as opposed to the MOCVD-grown samples where C is supplied by the CCl$_4$. All of the MOMBE-grown GaAs layers were grown at a substrate temperature of approximately 590°C, and the carbon concentration was controlled by varying the As$_2$/TMGa ratio. All growths were carried out on semi-insulating GaAs (100) substrates. Layer thicknesses were between 0.47 and 0.79 µm, as determined from RHEED oscillations during growth, and by surface profilometry measurement of SIMS crater depths. The sample with the highest carbon concentration was grown with the lowest possible $V/III$ ratio while maintaining an As-stabilized surface during growth, as determined from the RHEED pattern. The surface morphology for the MOMBE-grown samples was specular in all cases. Be-doped GaAs samples were grown in the same system, using solid Ga and precracked AsH$_3$ as sources. These samples were $\approx 1.0$ µm thick, and were used to provide comparison between C-doped and Be-doped GaAs.

Variable temperature van der Pauw–Hall effect measurements were performed on samples covering the doping range from $1 \times 10^{17}$ cm$^{-3}$ to $1.5 \times 10^{20}$ cm$^{-3}$. Samples were cleaved to a size of 6 mm x 6 mm from the as-grown wafer, and 15 mil In/Zn spheres were alloyed at 300°C to form ohmic contacts at the sample corners. Several of the most heavily doped layers were measured with alloyed and non-alloyed ohmic contacts, and the alloying process was found to have no effect on the Hall effect results. The magnetic field was 6.5 kG, and a liquid He cooled cryostat was used for temperature control. All samples were slowly cooled to 4.2 K, and then 30 data points at different temperatures were taken as the sample temperature was increased in steps to 300 K.

SIMS depth profiles were obtained for the C-doped samples with hole concentrations in excess of $4 \times 10^{19}$ cm$^{-2}$ using a Cameca IMS-3f instrument, with a Cs$^+$ primary ion beam and negative secondary ion detection. Total carbon concentrations were deduced by comparing the depth profiles to those from a GaAs substrate that was ion-implanted with $^{12}$C at an energy of 125 keV and dose of $2 \times 10^{15}$ cm$^{-2}$. All GaAs samples with a carbon concentration in excess of $10^{19}$ cm$^{-3}$ have been analyzed using double crystal x-ray diffraction (DCXD) with CuK$_\alpha$ radiation. The (400) Bragg reflection was employed to determine the lattice mismatch. Plan-view TEM was used to look for evidence of formation of carbon precipitates or misfit dislocations due to strain relaxation in the most heavily doped epitaxial films. Plan-view specimens were prepared for TEM analysis by chemical etching from the substrate side until perforation.

**RESULTS AND DISCUSSION**

The variable temperature Hall effect data obtained for seven C-doped GaAs layers are summarized in Figs. 1 and 2. The mobility for the least heavily doped sample [sample A, $p(300\, \text{K}) = 2.0 \times 10^{17}$ cm$^{-2}$] increases as the temperature is decreased from 300 to about 80 K, as shown in Fig. 1(a), due to a decrease in phonon scattering. The hole concentration decreases as the temperature is lowered due to freezeout of holes onto acceptor sites, as can be seen in Fig. 2(a). As the temperature is lowered below 80 K the mobility decreases due to increased ionized impurity scattering and the fact that hopping conduction becomes dominant. The freezeout of carriers and the decrease in mobility result in high resistivity material for $T \lessgtr 80$ K as shown in Fig. 2(b). For temperatures below 20 K, the small activation energy associated with the resistivity is indicative of hopping conduction.

Phonon scattering is also important for temperatures greater than 100 K for sample B ($p = 9.7 \times 10^{17}$ cm$^{-2}$), and for $T < 70$ K, ionized impurity scattering is the...
FIG. 1. Hole mobility as a function of temperature for C-doped GaAs: (a) samples grown by MOCVD [300 K hole concentrations are $\rho(A) = 2.0 \times 10^{17}$ cm$^{-3}$, $\rho(B) = 9.7 \times 10^{17}$ cm$^{-3}$, $\rho(C) = 4.4 \times 10^{18}$ cm$^{-3}$, $\rho(D) = 1.6 \times 10^{19}$ cm$^{-3}$], and (b) samples grown by MOMBE [$\rho(E) = 6.5 \times 10^{19}$ cm$^{-3}$, $\rho(F) = 8.4 \times 10^{19}$ cm$^{-3}$, $\rho(G) = 1.4 \times 10^{20}$ cm$^{-3}$].

dominant mobility-limiting mechanism. The hole concentration reaches a minimum of $\approx 5 \times 10^{17}$ cm$^{-3}$ at 70 K, and then appears to increase at lower temperatures, indicating that the carbon acceptors are close enough for impurity band conduction to occur. This impurity band conduction is also evidenced by the variation of resistivity with temperature, shown in Fig. 2(b). The mobility for sample B becomes nearly constant for $T < 20$ K as the sample becomes degenerate.

For sample C ($\rho = 4.4 \times 10^{18}$ cm$^{-3}$), both phonon scattering and ionized impurity scattering are important at temperatures above 100 K. No carrier freezeout is observed for this sample, indicating that the impurity band and valence bands have effectively merged to form a continuum of states. This conclusion is supported by room temperature photoluminescence data which indicate that the effective band gap is reduced by about 25 meV as the doping is increased in a very narrow range from $1.5 \times 10^{18}$ to $4.4 \times 10^{18}$ cm$^{-3}$. This change in energy gap is approximately equal to the carbon acceptor ionization energy of 26 meV. For $T < 100$ K, the sample is degenerate, and the ionized impurity scattering-limited mobility becomes nearly constant. This "degenerate conduction," where the ionized impurity scattering is independent of $T$, is similar to the behavior seen in metals. A temperature-independent mobility has been previously observed by many workers, and has been theoretically described for degenerately doped $n$-type GaAs.$^{14}$

Degenerate conduction is dominant over the entire temperature range studied when $\rho > 10^{19}$ cm$^{-3}$, as observed for samples D ($\rho = 1.6 \times 10^{19}$ cm$^{-3}$). At low temperatures, the mobility is dominated by ionized impurity scattering and is independent of temperature. At higher temperatures, the total mobility may be roughly estimated by combining the effects of ionized impurity and phonon scattering according to Matthiesen's rule to get

$$\frac{1}{\mu} \approx \frac{1}{\mu_{\text{II}}} + \frac{1}{\mu_{\text{lat}}(T)},$$

where $\mu_{\text{lat}}(T) \approx \mu_{\text{i}} \left( \frac{297K}{T} \right)^{\alpha}$.

Through variable temperature Hall effect analysis of high-purity $p$-type MBE-grown GaAs, we have determined that $\mu_{\text{i}} \approx 435$ cm$^2$/V s and $\alpha \approx 2.37$ for GaAs. An attempt was made to fit the data from sample D using the measured
mobility at 4.2 K as $\mu_{II}$, and the values of $\mu_1$ and $\alpha$ given above. The calculated mobilities were found to be about 15% higher than those measured between 200 and 300 K.

Figure 1(b) shows the Hall mobility as a function of temperature for several C-doped GaAs layers grown by MOMBE (samples E, F, and G). Carrier freezeout is not observed in these highly degenerate samples, as seen in Fig. 2(a). All MOMBE-grown samples measured had hole concentrations of $6 \times 10^{19}$ cm$^{-3}$ or higher and exhibited temperature-dependent behavior similar to that observed for the most heavily doped MOCVD-grown sample. The 77 K mobility in C-doped samples where $p > 10^{19}$ cm$^{-3}$ is typically 50% to 60% higher than at room temperature. The expression for total mobility described above shows good agreement with the measured data when using $\alpha \approx 1.5$ and values for $\mu_1$ that range from 250 cm$^2$/V s when $p = 1 \times 10^{19}$ cm$^{-3}$ to 150 cm$^2$/V s when $p = 1.4 \times 10^{20}$ cm$^{-3}$.

While Matthiesen’s rule is expected to provide only a crude approximation to the total mobility, the trends described above may be explained by simple arguments. The temperature exponent $\alpha$ for the lattice-limited mobility is about 1.5 for nondegenerate optical and acoustic phonon scattering. A decrease in the coefficient $\mu_1$ with increasing acceptor concentration is expected since $\mu_1$ for phonon scattering is inversely related to the effective mass. The hole effective mass may increase with increasing acceptor concentration due to a merging of the acceptor states with the top of the light and heavy hole valence bands, and also due to the position of the Fermi energy within the nonparabolic valence band in degenerately doped material. This change in effective mass is also evidenced by the fact that the low-temperature (4.2 K) mobility, which has been assumed to be equal to $\mu_{II}$, decreases with increasing doping. Comparison of Hall and SIMS data (data not shown) suggests that samples A–F are not highly compensated, so increased scattering due to ionized donors cannot be responsible for the reduction in $\mu_{II}$. Sample G may be slightly compensated, as will be discussed later. An expression for $\mu_1$ for degenerately doped material predicts that $\mu_{II}$ is independent of temperature, but is inversely proportional to $m^2$.

The above discussion is not intended as a quantitative explanation of the conduction in degenerately doped materials, but rather as a qualitative argument supporting the conclusion that the conduction is dominated by heavily screened ionized impurity scattering at low temperatures and is influenced by phonon scattering at higher temperatures. The important trend is that the mobility is significantly higher at 77 K and below than at room temperature for the heavily doped samples.

Several Be-doped GaAs samples with $1 \times 10^{19} < p < 6 \times 10^{19}$ cm$^{-3}$ were also characterized by variable temperature Hall effect measurements. The dependence of mobility on temperature was consistent with the arguments presented above. The major difference observed between the Be- and C-doped samples was that the mobility of C-doped samples was $\approx 20\%$–$30\%$ higher than for Be-doped layers with the same doping concentrations over the entire temperature range studied. Variable temperature Hall measurements have previously been performed by other researchers on p-GaAs where $p < 2 \times 10^{19}$ cm$^{-3}$. The trends noted here for C-doped GaAs are in good qualitative agreement with those previously observed when column II acceptors are used as the p-type dopant.

The 300 and 77 K mobilities for C-doped GaAs grown by MOCVD and MOMBE are summarized in Fig. 3. The solid line is a fit to our room temperature data, and the bend near $p = 10^{19}$ cm$^{-3}$ is due to the fact that the samples become degenerate at 300 K for $p > 10^{19}$ cm$^{-3}$. Even for $p > 10^{19}$ cm$^{-3}$, a significant reduction in resistivity may be gained by lowering the lattice temperature to 77 K. For an HBT, the maximum frequency of oscillation for unity power gain ($f_{max}$) is proportional to $1/(2\pi R C)^{1/2}$. Thus, the 50% increase in mobility associated with lowering the temperature from 300 to 77 K may translate into a significant increase in $f_{max}$.

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TABLE I. Various measured properties of four C-doped GaAs layers grown by MOMBE.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>p (300 K) (10^19 cm⁻³)</th>
<th>[C] (10¹⁹ cm⁻³)</th>
<th>μ (300 K) (cm²/V s)</th>
<th>μ (77 K) (cm²/V s)</th>
<th>Δa/a</th>
<th>Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>6.5</td>
<td>7</td>
<td>78</td>
<td>119</td>
<td>-1.1×10⁻³</td>
<td>0.47</td>
</tr>
<tr>
<td>F</td>
<td>8.4</td>
<td>7</td>
<td>73</td>
<td>111</td>
<td>-1.3×10⁻³</td>
<td>0.76</td>
</tr>
<tr>
<td>G</td>
<td>14.0</td>
<td>17</td>
<td>60</td>
<td>96</td>
<td>-1.8×10⁻³</td>
<td>0.79</td>
</tr>
<tr>
<td>H</td>
<td>10.5</td>
<td>18</td>
<td>57</td>
<td>85</td>
<td>-1.5×10⁻³</td>
<td>0.57</td>
</tr>
</tbody>
</table>

The as-grown 300 K hole concentration is plotted versus the total carbon concentration deduced from SIMS for samples with carbon concentrations in excess of 4×10¹⁹ cm⁻³ in Fig. 5. The total carbon concentration was found to increase monotonically with decreasing V/III ratio for GaAs grown by both MOCVD and MOMBE, as expected. When [C] > 4×10¹⁹ cm⁻³ in MOCVD-grown GaAs, the 300 K hole concentration is significantly lower than the measured carbon concentration. For [C] > 1.4×10²⁰ cm⁻³, we have found p(300 K) to be as much as 50% lower than [C]. Hydrogen has been detected in heavily carbon-doped GaAs grown by MOMBE and MOCVD at concentrations exceeding 10¹⁹ cm⁻³, and could be partially responsible for the observed difference between p(300 K) and [C] in this study.

The samples that have the largest discrepancy between [C] and p also exhibit the lowest hole mobilities. The mobilities for the MOMBE-grown samples are tabulated in Table I. The samples are labeled E, F, G, and H, in order of decreasing V/III ratio during growth. Sample H was grown with the lowest possible V/III ratio while still maintaining an As-stabilized surface, as determined from the RHEED pattern. Sample H, which was grown with the lowest V/III ratio, has a lower mobility and a lower hole concentration than sample G, so adding more carbon actually increased the resistivity in this case. This indicates that the excess carbon may play a role in degrading the hole conduction in these layers. This could be due to scattering by ionized substitutional or interstitial carbon donors (compensation), or to scattering by defects associated with dislocations or neutral interstitial carbon atoms.

Vegard's law was used to calculate the expected mismatch (Δa/a) as a function of carbon concentration, assuming a carbon covalent bonding radius of 0.77 Å, and that all the carbon is substitutional on the As sublattice. The covalent bonding radii of Ga and As (1.26 and 1.20 Å, respectively) are nearly equal, so the calculation is relatively insensitive to the exact site of the carbon, provided that it is all substitutional. The expected lattice contraction for a coherently strained epitaxial layer was also calculated, assuming a Poisson ratio of 0.31. The lattice mismatch of MOCVD-grown samples with carbon concentrations ranging from 1×10¹⁵ cm⁻³ to 2.6×10²⁰ cm⁻³ was determined by DCXD, and found to be roughly in agreement with the mismatch predicted for strained epitaxial layers. All layers of 0.75 μm or less showed no signs of cross-hatching when viewed using Nomarski interference contrast microscopy. However, MOCVD-grown samples...
heavily C-doped GaAs grown by MOCVD and MOMBE. The solid curves were calculated using Vegard's law for the cases of a coherently strained and a fully relaxed epitaxial layer. The labels for the three MOCVD-grown samples with \([\text{C}]=1.8 \times 10^{20} \text{ cm}^{-3}\) correspond to the epilayer thicknesses.

<table>
<thead>
<tr>
<th>Thickness ((\mu)m)</th>
<th>MOCVD</th>
<th>MOMBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9</td>
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</table>

\(\Delta a/a\) as a function of total carbon concentration for heavily C-doped GaAs grown by MOCVD and MOMBE. The solid curves were calculated using Vegard's law for the cases of a coherently strained and a fully relaxed epitaxial layer. The labels for the three MOCVD-grown samples with \([\text{C}]=1.8 \times 10^{20} \text{ cm}^{-3}\) correspond to the epilayer thicknesses.

FIG. 6. Lattice contraction as a function of total carbon concentration for heavily C-doped GaAs grown by MOCVD and MOMBE. The solid curves were calculated using Vegard's law for the cases of a coherently strained and a fully relaxed epitaxial layer. The labels for the three MOCVD-grown samples with \([\text{C}]=1.8 \times 10^{20} \text{ cm}^{-3}\) correspond to the epilayer thicknesses.

nearly the same as that measured for samples as thin as 0.3 \(\mu\)m and in approximate agreement with Vegard's law, as shown in Fig. 6. Thus, DCXD was not found to be a sensitive technique for detecting strain relaxation in the samples grown by MOCVD.

The variation of the measured lattice mismatch with total carbon concentration for the four MOMBE-grown layers is also shown in Fig. 6. The two most heavily doped samples (G and II in Table 1) have a smaller mismatch than predicted by Vegard's law for strained epitaxial layers. These layers exhibit excellent surface morphology and no evidence of cross-hatching when analyzed using Nomarski interference contrast microscopy. Further evidence that the layers have not relaxed is provided by plan-view transmission electron microscopy (TEM) analysis which shows no evidence of dislocations. Although this does not preclude the possibility of partial lattice relaxation, it does suggest that the dislocation density is low enough (\(<10^5 \text{ cm}^{-2}\)) that it should not significantly affect majority carrier transport in these heavily doped layers.

The theoretical curves in Fig. 6 effectively represent the expected mismatch for a given substitutional carbon concentration. If all the carbon in sample H was substitutional (Ga and/or As sites) and the lattice was strained, then the lattice mismatch should be approximately twice that actually observed. Two possible explanations for this discrepancy must be considered. The first is that partial lattice relaxation has occurred, causing the mismatch to fall close to that predicted for a fully relaxed epitaxial layer. Calculation of the expected critical thickness according to the theoretical model of Matthews and Blakeslee predicts that layers G and H should be relaxed. However, many of the MOCVD-grown samples discussed above also exceed the calculated critical thickness, while the degree of lattice contraction appears to suggest relaxation has not occurred in some of these layers. The second possibility is that a large fraction of the carbon in sample H occupies interstitial sites and thus does not contribute to contraction of the lattice.

Several aspects of the investigation into the site location of carbon in the MOMBE-grown GaAs samples are currently under study.\(^{22}\) The fact that sample H has a lower hole concentration than sample G may be due to a lower concentration of carbon acceptors due to thermodynamic factors during growth, or due to hydrogen passivation or some sort of carbon self-compensation. In the case of self-compensation, then substitutional carbon donors or ionized interstitial (donor-like) carbon may be responsible. While the lattice contraction data presented above do not support an explanation based solely on substitutional carbon donors, some sort of self-compensation involving interstitial carbon seems plausible. No evidence of large carbon precipitates (>50 Å) was observed during TEM analysis, so precipitation is not viewed as a likely explanation for the apparent saturation of hole concentration with decreasing \(V/III\) ratio.

SUMMARY AND CONCLUSIONS

Variable temperature Hall analysis of C-doped GaAs has shown that for \(p > 1 \times 10^{19} \text{ cm}^{-3}\), "degenerate" or "metallic" conduction is dominant. The mobility limiting scattering mechanism at low temperatures is a temperature-independent ionized impurity scattering, while for \(T > 100 \text{ K}\) phonon scattering is also important. The 77 K hole mobility is typically 50% to 60% higher than at room temperature when \(p > 10^{19} \text{ cm}^{-3}\), resulting in 35% decrease in resistivity compared to that at room temperature. This effect is important for modeling \(n-p-n\) HBT device performance at cryogenic temperatures, since the external base resistance is a critical parameter influencing high-frequency performance. For hole concentrations of less than 10^18 cm^-3, hole freezeout results in highly resistive material at low temperatures.

The room temperature hole mobilities for C-doped GaAs are similar to those obtained by Zn- and Be-doping of GaAs for \(p < 2 \times 10^{18} \text{ cm}^{-3}\). However, when the hole concentration exceeds 2 \times 10^{18} cm^-3 the hole mobilities achievable using carbon as a dopant are significantly higher than for Be or Zn. MOCVD and MOMBE have been found to be capable of producing C-doped \(p^+\)-GaAs with similar mobilities, indicating that neither technique has an advantage over the other for producing low-resistivity material. For \(p > 10^{20} \text{ cm}^{-3}\), the hole mobility is observed to decrease abruptly with increasing carbon concentration. This may be related to the presence of excess carbon in the lattice, as measured by SIMS.

SIMS and Hall effect measurements have shown that a large fraction of the carbon in as-grown samples doped higher than 4 \times 10^{19} cm^-3 is electrically inactive. DCXD analysis shows good agreement with Vegard's law for coherently strained epilayers. However, in the case of MOMBE-grown GaAs doped in excess of 1 \times 10^{20} cm^-3, the mismatch is significantly lower than predicted. A high concentration of excess carbon, some of which may occupy interstitial sites, raises the possibility of a higher diffusion coefficient for atomic carbon in GaAs for \([\text{C}] > 4 \times 10^{19}\)
than has been measured at lower concentrations. The
derg of strain and lattice relaxation in these epitaxial
layers also remains uncertain, and its effect upon device
performance requires further study.

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6P. Enquist, J. A. Hutchby, and T. J. deLyon, J. Appl. Phys. 63, 4485
(1988).
8B. T. Cunningham, M. A. Haase, M. J. McCollum, J. E. Baker, and G.
9N. Kihayashi, T. Makimoto, and Y. Horikoshi, Appl. Phys. Lett. 50,
10B. T. Cunningham, L. J. Guido, J. E. Baker, J. S. Major, Jr., N. Hol-
11M. Konagai, T. Yamada, T. Akatsuka, K. Saito, E. Tokumitsu, and K.
13B. T. Cunningham, J. E. Baker, S. A. Stockman, and G. E. Stillman,
14D. M. Szymy, M. C. Hanna, and A. Majerfeld, J. Appl. Phys. 68, 2376
15S. A. Stockman, M. J. McCollum, and G. E. Stillman (unpublished
data).
16J. D. Wiley, in Semiconductors and Semimetals, edited by R. K.
91.
18M. C. Hanna, Z. H. Lu, and A. Majerfeld, Appl. Phys. Lett. 58, 164
19D. M. Kozuch, M. Stavola, S. J. Pearton, C. R. Abernathy, and J.
20G. E. Fernandez-Hüller, K. C. Hsieh, and N. Holonyak, Jr., Electronic
21J. W. Matthews, A. E. Blakeslee, and S. Mader, Thin Solid Films 33,
255 (1976).
22G. E. Hüller, J. N. Baillargeon, J. L. Klatt, K. C. Hsieh, R. S. Aver-
back, and K. Y. Cheng, in GaAs and Related Compounds 1991, Seattle,
WA, edited by G. B. Stringfellow (Institute of Physics, Bristol, 1992),
IOP Conf. Ser. No. 120, p. 631.

987 J. Appl. Phys., Vol. 72, No. 3, 1 August 1992 Stockman et al. 987