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A Comparison of TMGa and TEGa for Low-Temperature Metalorganic Chemical Vapor Deposition Growth of CCl_4-Doped InGaAs

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Factors which influence the alloy composition and doping level of CCl_4-doped $In_{0.53}Ga_{0.47}As$ grown at low temperatures (450°C < T_g < 560°C) by low-pressure metalorganic chemical vapor deposition (MOCVD) have been investigated. The composition is highly dependent on substrate temperature due to the preferential etching of In from the surface during growth and the temperature-dependent growth efficiency associated with the Ga source. The lower pyrolysis temperature of TEGa relative to TMGa allows the growth of CCl_4-doped InGaAs at lower growth temperatures than can be achieved using TMGa, and results in improved uniformity. High p-type doping ($p \sim 7 \times 10^{19}$ cm^{-3}) has been achieved in C-doped InGaAs grown at T_g = 450°C. Secondary ion mass spectrometry analysis of a C-doping spike in InGaAs before and after annealing at ~670°C suggests that the diffusivity of C is significantly lower than for Zn in InGaAs. The hole mobilities and electron diffusion lengths in p^+-InGaAs doped with C are also found to be comparable to those for Be and Zn-doped InGaAs, although it is also found that layers which are highly passivated by hydrogen suffer a degradation in hole mobility. InP/InGaAs heterojunction bipolar transistors (HBTs) with a C-doped base exhibit high-frequency performance (f_t = 62 GHz, f_{max} = 42 GHz) comparable to the best reported results for MOCVD-grown InP-based HBTs. These results demonstrate that in spite of the drawbacks related to compositional nonuniformity and hydrogen passivation in CCl_4-doped InGaAs grown by MOCVD, the use of C as a stable p-type dopant and as an alternative to Be and Zn in InP/InGaAs HBTs appears promising.

Key words: C-doping, InGaAs, metalorganic chemical vapor deposition (MOCVD)

INTRODUCTION

Carbon has been widely adopted as a p-type dopant for AlGaAs/GaAs device structures grown by metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). For MOCVD-grown GaAs, CCl_4 has proven to be a particularly effective and convenient doping source.[1,2] However, it has been reported to act primarily as an etchant for InP and InGaP.[3] The principal advantage of C over other acceptor species in GaAs (Be and Zn) is its extremely low atomic diffusion coefficient.[4,5] This low diffusivity makes C an ideal choice for the base dopant in AlGaAs/GaAs heterojunction bipolar transistors (HBTs),[6] where unintentional redistribution of the base dopant during crystal growth, device fabrication, or device operation can severely affect device performance. Recent work has shown that AlGaAs/GaAs HBTs with a heavily carbon-doped base exhibit more stable operating characteristics under high bias at elevated temperature than is observed for HBTs with a Be-doped base.[7] Thus, carbon has become the preferred base dopant for high-reliability GaAs-based

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HBTs, and the development of C as an alternative to Zn has made practical the growth of reliable AlGaAs/GaAs HBTs by MOCVD.

High performance InP/InGaAs HBTs with a Be-doped base grown by gas-source MBE have been demonstrated,[8] and high speed integrated circuits have been fabricated from MBE-grown InAlAs/InGaAs HBTs.[9] Promising results have also been published for InP/InGaAs HBTs grown by MOCVD with a Zn-doped base,[10,11] but the high diffusivity of Zn currently limits the usefulness of MOCVD for production of highly-reliable HBTs. While carbon doping has had an important impact on GaAs-based HBT technology, the amphoteric behavior of C and difficulty in incorporation of C in In-containing materials has inhibited the development of C-doping of InGaAs.[12,13] Recently, Chin et al. have demonstrated heavy p-type doping ($p = 3 \times 10^{19}$ cm^{-3}) of $In_{0.53}Ga_{0.47}As$ using CCl_4 by MBE[14] and have reported on the dc characteristics of InP/InGaAs HBTs with a C-doped base.[15] We have previously demonstrated p-type doping ($p = 1 \times 10^{19}$ cm^{-3}) of $In_{0.53}Ga_{0.47}As$ by MOCVD[16] and have described the dc characteristics of HBTs[17] and the effects of incorporation of hydrogen during growth and during the post-growth cool-down.[18]

In this paper, we report on factors which influence the alloy composition, uniformity, and doping level of CCl_4-doped InGaAs grown by MOCVD. The lower pyrolysis temperature of TEGa relative to TMGa allows growth at very low temperatures, resulting in improved uniformity and higher p-type doping ($p \sim 7 \times 10^{19}$ cm^{-3}). We also show that the diffusivity of C is lower than for Zn in InGaAs. The electrical quality of C-doped InGaAs is characterized in terms of majority and minority carrier transport, and high-frequency InP/InGaAs HBTs are demonstrated.

GROWTH

Growth Conditions

All growths for this study were performed on semi-insulating (100) InP substrates misoriented two degrees toward (110). The growth precursors were PH_3, AsH_3, TMIn, and TMGa or TEGa. Dopant sources were Si_2H_6 and CCl_4, and all growths were carried out at a reactor pressure of 76 Torr and a total H_2 flow rate of 10 slm. Carbon doped InGaAs layers were grown at low V/III ratio (as low as V/III ~5) and in the temperature range of T_g = 450 to 560°C. A modified Emcore GS3100 vertical growth chamber was employed, with a substrate rotation rate of 1000 rpm. InP/InGaAs HBT structures were grown on 2 in substrates, and the axis of rotation for the wafer was coincident with the center of the wafer. The substrate temperature was estimated using a thermocouple located beneath the rotating Mo susceptor and was calibrated at the Al/Si eutectic temperature (577°C). The susceptor was heated from below by a graphite resistance heater. A slight radial nonuniformity in temperature (about 5°C ± 2°C from the center to the wafer edge) was verified by observation of the formation of the Al/Si eutectic on 2 in silicon substrates.

Preliminary data on the growth of CCl_4-doped InGaAs using TMIn, TMGa, AsH_3, and CCl_4 has been reported previously.[16] We found that the $In_xGa_{1-x}As$ alloy composition (x) was highly dependent on CCl_4 partial pressure, V/III ratio, and growth temperature and speculated that etching of In from the surface via chlorine-containing compounds during growth was responsible for this behavior. Kibbler et al. had earlier noted similar behavior during atmospheric pressure MOCVD growth of InGaP at 600°C, and suggested that etching by HCl occurred during growth.[3] In the case of InGaAs, we found that etching could be reduced and carbon incorporation enhanced by growing at low temperatures (~500°C).[16]

Significant incorporation of hydrogen has also been observed during MOCVD growth of C-doped InGaAs, and during the cooling stage after growth is complete.[18] This results in passivation of the carbon acceptors, lowering the p-type doping level by as much as 90%. In the case of hydrogen incorporation during growth, the degree of passivation increases with decreasing growth temperature. The post-growth cooling ambient (AsH_3 and H_2) was also found to influence the degree of passivation in uncapped C-doped InGaAs layers. The hydrogen passivation can be reversed by post-growth annealing in a hydrogen-free environment at ~400°C, thereby increasing the hole concentration. However, in the case of an n-p-n HBT, we have found that hydrogen cannot be annealed out of the buried p-type base layer at 400°C, presumably due to blocking of the diffusion of H^+ by the built-in electric fields at the base-collector and base-emitter p-n junctions.[18]

CCl_4 Etching

The use of CCl_4 as a dopant source for GaAs results in a reduced growth rate due to formation of volatile gallium chlorides at the GaAs surface during growth.[19] We have directly measured the etch rates for GaAs and InAs in the MOCVD reactor using CCl_4 under conditions similar to growth. InAs and GaAs substrates were capped with SiO_2 using a low-temperature plasma-enhanced chemical vapor deposition (PECVD) process. Standard photolithographic procedures were then used to define SiO_2 dots, which were used as a mask for the CCl_4 etching of the substrates. Samples were etched in the MOCVD reactor by injecting CCl_4 under typical growth conditions (AsH_3 flow and substrate temperature), except for the absence of column III sources. After etching with CCl_4, the SiO_2 was removed using a buffered HF solution, and the etched depth was measured using a surface profilometer.

The etch rates for InAs and GaAs are plotted as a function of reciprocal temperature in Fig. 1 for CCl_4 and AsH_3 flow rates of 4.5×10^{-6} mol/min and 1.1×10^{-3} mol/min, respectively. The etch rate for InAs is significantly higher than for GaAs and is highly dependent on substrate temperature. The etching has also been studied as a function of CCl_4 and AsH_3 partial pressures, and the etch rate can be described by:

$$R_{etch} \propto \frac{[CCl_4]}{\sqrt{[AsH_3]}} e^{-(1.7eV)/kT} \qquad (1)$$

This empirical description of the etch rate suggests a reaction of the form:

$$HCl + InAs \rightarrow InCl + 1/2\, As_2 + 1/2\, H_2 \qquad (2)$$

This reaction is the reverse of chloride-transport vapor phase epitaxy and is consistent with the analysis of Kibbler et al. in describing the etching of InP by CCl_4.[3] We have not verified the presence of HCl in the reactor, and Eq. (2) is just one possible reaction which could contribute to the observed etching. We have found no evidence of significant gas-phase reaction between CCl_4 and the organometallic column III sources.

Etching also occurs during growth of CCl_4-doped InGaAs, resulting in a reduced incorporation efficiency for In. This makes it necessary to use a higher TMIn flow for growth of CCl_4-doped $In_{0.53}Ga_{0.47}As$ than is used for growth of undoped $In_{0.53}Ga_{0.47}As$ at growth temperatures of 575°C or higher. The reduction in In incorporation during growth of $In_xGa_{1-x}As$ ($x \sim 0.53$) is about 25% smaller than one would predict based on the etch rate of InAs. No evidence of a direct reaction between CCl_4 and organometallics has been observed, so we attribute this to a reduction in the effective etch rate due to partial occupancy of the column III surface sites by Ga. For temperatures of less than 550°C, the GaAs etch rate is low enough that we will assume in the discussion below it is negligible compared to the etch rate of InAs and the growth rate of InGaAs.

We have found that the incorporation of carbon in InGaAs is approximately proportional to the CCl_4 partial pressure ($[CCl_4]$), and inversely proportional to the AsH_3 partial pressure ($[AsH_3]$). This trend is similar to that observed in GaAs, with the exception that much lower growth temperatures are required to achieve significant C concentrations in InGaAs. However, a high $[CCl_4]$ and low V/III ratio (low $[AsH_3]$) also contribute to rapid etching of In from the surface during growth, as shown in Eq. (1), making compositional control difficult. Thus, a trade-off between C incorporation and etch rate must be considered when choosing the CCl_4 flow rate and V/III ratio.

The incorporation of C in InGaAs has also been found to be extremely temperature-dependent. Low substrate temperatures result in increased carbon doping levels. The etch rate also decreases with decreasing temperature, so high C incorporation and low etch rates can be achieved simultaneously by growing CCl_4-doped InGaAs at low substrate temperatures ($T_g < 550$°C).

Control of Alloy Composition

Many authors have reported that the growth of GaAs using TMGa and AsH_3 is mass-transport-limited for temperatures greater than 575°C. For $T_g < 575$°C, however, the growth rate decreases with decreasing temperature due to limitations associated with surface kinetics, i.e., the growth of GaAs becomes kinetically limited.[20] For the case of CCl_4-doped InGaAs, a substrate temperature below 550°C is necessary to achieve efficient incorporation of C and In, as described above. This makes it necessary to grow the ternary alloy InGaAs in the kinetically limited growth regime. The lower thermal stability of TEGa relative to TMGa enables mass-transport-limited growth of GaAs at lower temperatures.[20] Thus, the incorporation of Ga from TEGa is more efficient and less sensitive to temperature than the incorporation of Ga from TMGa at temperatures below 575°C. This is qualitatively illustrated in Fig. 2a, where the relative deposition rate (growth rate) is plotted vs temperature.

The MOCVD growth of InP and InAs using TMIn ($In(CH_3)_3$) is generally mass-transport-limited at lower temperatures than for GaAs using TMGa ($Ga(CH_3)_3$) due to the fact that the $In\text{-}CH_3$ bond is weaker than the $Ga\text{-}CH_3$ bond.[21] In the case of heavily CCl_4-doped InGaAs, however, the CCl_4 partial pressure is comparable to the TMIn partial pressure, and the In incorporation is effectively reduced by the etching reaction described above. This results in a decrease in the In incorporation efficiency with increasing substrate temperature, as illustrated in Fig. 2b (the Ga incorporation decreases only slightly due to etching, and this decrease is ignored in Fig. 2b). The alloy composition of InGaAs grown under these conditions is highly temperature-dependent due to the fact that In incorporation becomes less efficient, while Ga incorporation becomes more efficient, with increasing temperature. For growth of heavily CCl_4-doped $In_xGa_{1-x}As$ ($x \sim 0.53$, $p_{annealed} \sim 1 \times 10^{19}\ cm^{-3}$) at $T_g \sim 520$°C, $R_g \sim 1.5\ \mu m/h$, and V/III ~5, using TMGa as the Ga source, the

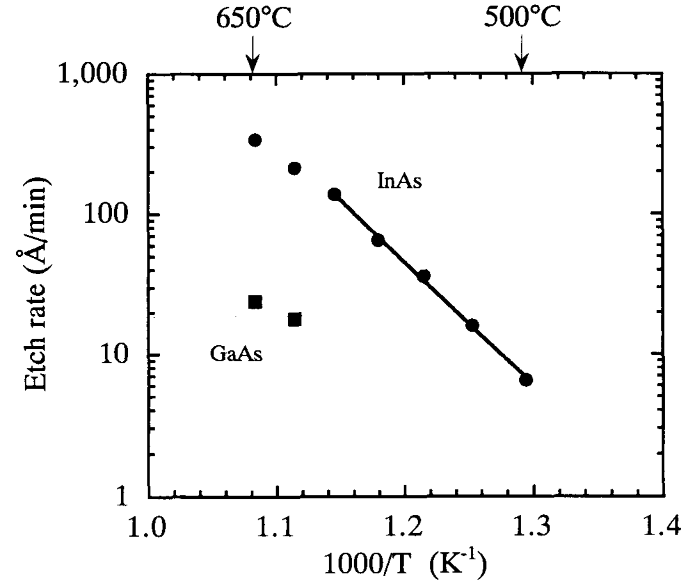

Fig. 1. Etch rate for (100) GaAs and InAs substrates in the presence of CCl_4 as a function of reciprocal temperature. The AsH_3 and CCl_4 partial pressures were typical of those used for growth of heavily C-doped GaAs. The InAs etch rate is significantly higher than that for GaAs.

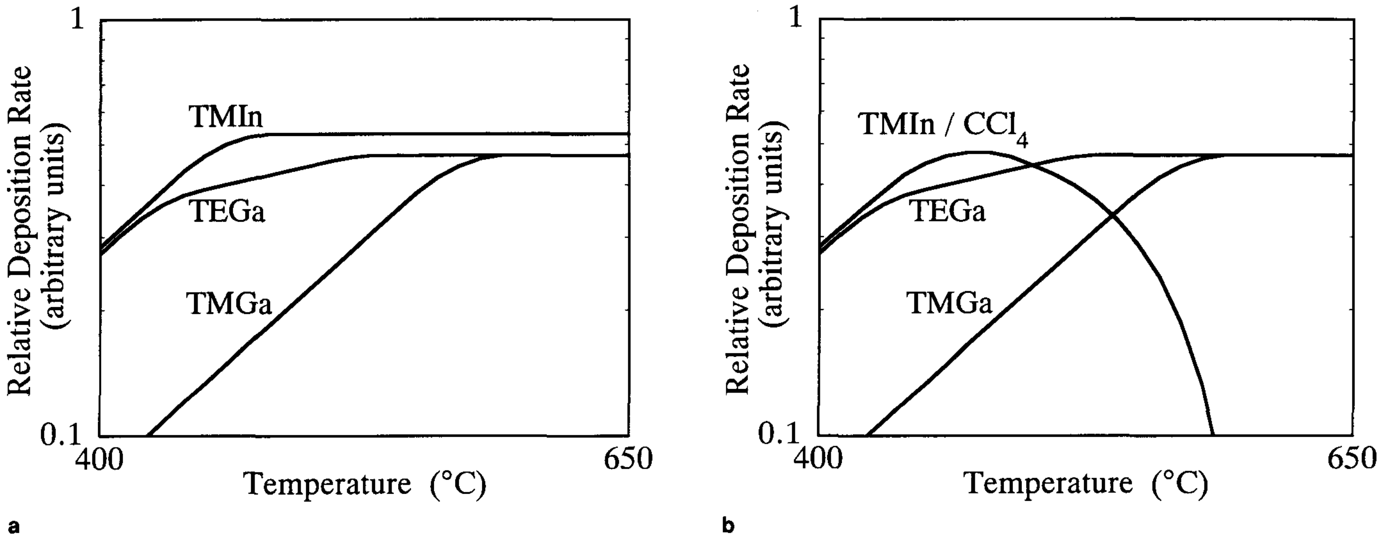

Fig. 2. (a) Qualitative description of the deposition rate (growth rate) associated with TMIn, TMGa, and TEGa as a function of temperature. The use of TEGa allows mass-transport-limited growth of GaAs and InGaAs at lower temperatures than can be achieved using TMGa. (b) The incorporation of In from TMIn is reduced under the conditions used for heavy carbon doping of InGaAs in this study, where the partial pressure of CCl_4 is comparable to that for TMIn. The preferential etching of In from the surface of an InGaAs epitaxial layer during growth reduces the InAs mole fraction in the layer. The etching can be reduced by growing at low temperatures (T <550°C) where the incorporation of Ga is limited by surface kinetics.

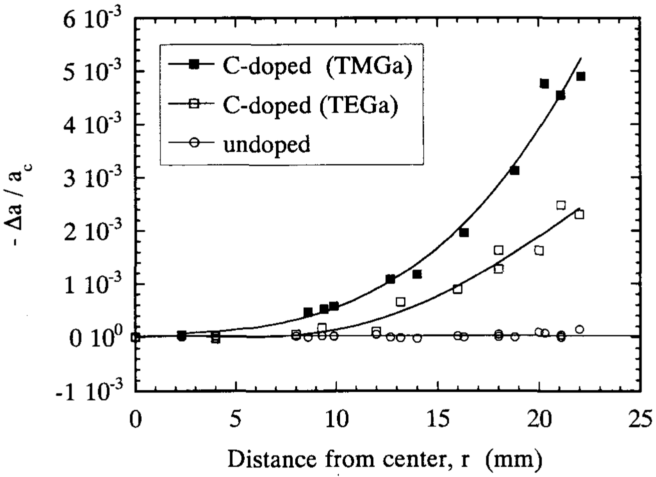

Fig. 3. Lattice mismatch with respect to the center of a 2 in diameter wafer for InGaAs grown on InP. For the case of undoped InGaAs grown at ~625°C, the composition is extremely uniform across the wafer, with a variation in $\Delta a/a_c$ of less than 1×10^{-4}. For the case of CCl_4-doped InGaAs grown using TMGa as the Ga source (T_g ~520°C, [C] ~1×10^{19} cm^{-3}), a severe compositional nonuniformity is apparent and is the result of a small variation in substrate temperature between the center and the edge of the wafer. When TEGa is used as the Ga source (T_g ~520°C, [C] ~1×10^{19} cm^{-3}), the uniformity is improved because the incorporation of Ga is less sensitive to temperature than when TMGa is employed as the Ga source.

lattice mismatch ($\Delta a/a$) changes by approximately -6×10^{-4} for an increase in substrate temperature of 1°C. This is equivalent to a change in composition with respect to growth temperature (T_g) of $\Delta x/\Delta T_g = -0.009$ (°C)$^{-1}$. Substitution of TEGa for TMGa under these conditions results in a reduction of the sensitivity of alloy composition to temperature. This is due to the fact that Ga incorporation is less temperature-dependent when using TEGa under these conditions, and $\Delta x/\Delta T_g = -0.005$ (°C)$^{-1}$ is measured.

The fact that the alloy composition (x) of CCl_4-doped $In_xGa_{1-x}As$ is dependent on the growth conditions (T_g, CCl_4 flow, AsH_3 flow) means that each time one of these parameters is changed to achieve a different doping level, the flow rate of TMIn or TMGa must also be adjusted to obtain x ~0.53. For the conditions used here, the dependence of x on T_g places severe restrictions on the degree of control over substrate temperature stability, reproducibility, and uniformity which are required in order to repeatably achieve lattice match to InP over large areas. Fluctuation in T_g of less than 1°C during growth of a thick (0.5–1.0 μm) CCl_4-doped InGaAs layer results in significant broadening of the epitaxial layer peak when the sample is analyzed using double crystal x-ray diffraction (DCXD). In addition, very tight control over T_g is required to achieve run-to-run reproducibility in terms of lattice match to InP.

Figure 3 shows the effect of a small variation in substrate temperature across a 2 in (50 mm) diameter InP wafer on the compositional uniformity for three cases. The lattice mismatch is plotted as $-\Delta a/a_c$, where a_c is the lattice constant of the epitaxial layer in the center of the wafer (r = 0 mm), rather than $-\Delta a/a_0$, where a_0 is the lattice constant of the InP substrate, so that changes in lattice constant across the wafer can be directly compared. The data was compiled from DCXD rocking curves taken at several locations on a series of HBT structures grown on 2 in InP substrates. The lattice mismatch of the subcollector/collector and the base region were then estimated by comparison with simulated curves obtained using dynamical x-ray diffraction theory.

For the case of undoped InGaAs grown at ~625°C (the collector region in the HBT), the composition is extremely uniform across the wafer, with a variation in $\Delta a/a_c$ of less than 1×10^{-4}. For the case of CCl_4-doped InGaAs (the base region) grown using TMGa as the Ga source (T_g ~520°C, V/III ~5, [C] ~1×10^{19} cm^{-3}), a severe compositional nonuniformity is apparent. This is primarily the result of the slight temperature nonuniformity described above. The substrate temperature is ~5°C (±2°C) higher near the edge (r ~ 22 mm) than at the center of the wafer (r = 0 mm). Thus, the CCl_4-doped layer has a lower InAs mole fraction (x) near the edge than at the center. When TEGa is substituted for TMGa for growth of the CCl_4-doped InGaAs base region, the compositional uniformity is improved. This is the result of the decreased sensitivity of composition to temperature, as described above. The base sheet resistance has also been measured across 2 in wafers, and it varies by less than 10% from r = 0 to r = 22 mm, suggesting that the doping level and thickness of the base are relatively constant.

We have demonstrated that the use of TEGa results in better reproducibility and uniformity of the composition of heavily CCl_4-doped InGaAs grown at T_g ~ 520°C. It is also apparent from Fig. 2b that the growth efficiency associated with TEGa is significantly higher than for TMGa when $T_g \leq 520°C$. Thus, the use of TEGa also allows growth of CCl_4-doped InGaAs at lower substrate temperatures, where C incorporation is more efficient.

Carbon Incorporation

Figure 4 shows the hole concentration as a function of growth temperature for CCl_4-doped $In_xGa_{1-x}As$ (x ~0.53) grown using TMGa or TEGa. The CCl_4 and TMIn molar flow rates were kept constant, and the flow of the Ga source was adjusted for each growth temperature to achieve lattice match to InP. When using TMGa under these conditions, lattice-matched epitaxial layers could be grown in the temperature range of $520°C \leq T_g \leq 560°C$. A maximum doping level of $p \sim 1 \times 10^{19}$ cm^{-3} was achieved for $T_g = 520°C$. The use of TEGa allowed growth at temperatures as low as $T_g = 450°C$, where a maximum doping level of $p \sim 7 \times 10^{19}$ cm^{-3} was achieved. All layers were grown at ~ 1.5 μm/h, and the dependence of carbon incorporation on growth rate was not studied.

It is clear from the data of Fig. 4 that the incorporation of C in InGaAs is highly dependent on the growth temperature. This trend is similar to that observed for GaAs and AlGaAs, for C incorporation from TMAs[4] and CCl_4,[1,2,22] except that much lower substrate temperatures are required to achieve high C incorporation during MOCVD growth of InGaAs. Buchan et al.[2] have proposed that the incorporation of C in GaAs from halomethane sources is controlled by competition between decomposition and desorption of adsorbed carbon-containing species, where both processes are temperature-dependent. We propose that in the case of CCl_4, the decomposition of adsorbed CCl_y ($1 \leq y \leq 4$) is not a rate-limiting factor for temperatures as low as 450°C. As shown in Fig. 4, the carbon incorporation is decreased for increasing substrate temperatures due to the increased desorption rate of the carbon-containing species. The low substrate temperatures required to obtain high concentrations of C acceptors in InGaAs relative to GaAs and AlGaAs can be explained by considering the relative strengths of the In-C, Ga-C, and Al-C bonds. The average bond strength for $In\text{-}CH_3$ (~47 kcal/mol) is significantly lower than for $Ga\text{-}CH_3$ (~59 kcal/mol) or $Al\text{-}CH_3$ (~66 kcal/mol) in the case of the metal alkyls TMIn, TMGa, and TMAl.[21,23] Desorption of CCl_y ($1 \leq y \leq 3$) is more efficient from an InGaAs surface than from GaAs, since the $In\text{-}CCl_y$ bond is weaker than $Ga\text{-}CCl_y$, leading to reduced incorporation of C acceptors (C on As sites). It has been reported that the addition of only a few percent In to GaAs to form $In_xGa_{1-x}As$ ($0 \leq x \leq 0.03$) can drastically reduce the incorporation efficiency of C during MOCVD growth at $T \geq 600°C$.[24] This behavior may be explained by the enhanced surface mobility of CCl_y ($1 \leq y \leq 3$) at higher substrate temperatures, and the efficient desorption of the carbon-containing species from a surface site where it is bonded to In, rather than Ga. These arguments may be extended to account for the efficiency of carbon incorporation which we have observed in the As-based materials[1,16,22] grown by MOCVD using CCl_4: $[C_{As}]_{AlAs} > [C_{As}]_{AlGaAs} > [C_{As}]_{GaAs} > [C_{As}]_{InGaAs}$.

CHARACTERIZATION

Carbon Diffusion

The major motivation for this work is that C exhibits a significantly lower thermal diffusion coefficient in the GaAs/AlGaAs materials system than the commonly used column II acceptors Be and Zn and is expected to behave similarly in other III-V materials such as InP/InGaAs. In the case of Zn-doped InGaAs grown by MOCVD, rapid redistribution (diffusion) of Zn occurs during growth when the Zn doping level approaches 10^{19} cm^{-3}. This redistribution complicates the growth of devices such as HBTs, where the precise

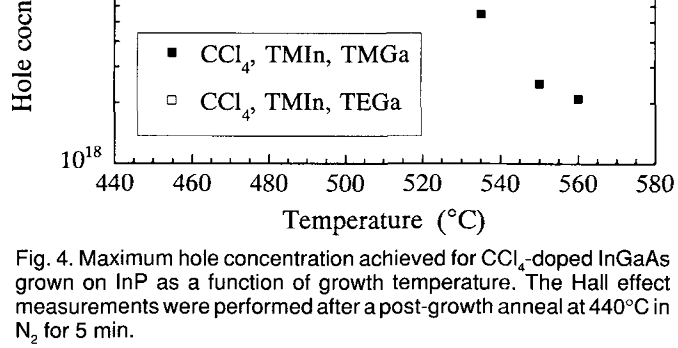

Fig. 4. Maximum hole concentration achieved for CCl_4-doped InGaAs grown on InP as a function of growth temperature. The Hall effect measurements were performed after a post-growth anneal at 440°C in N_2 for 5 min.

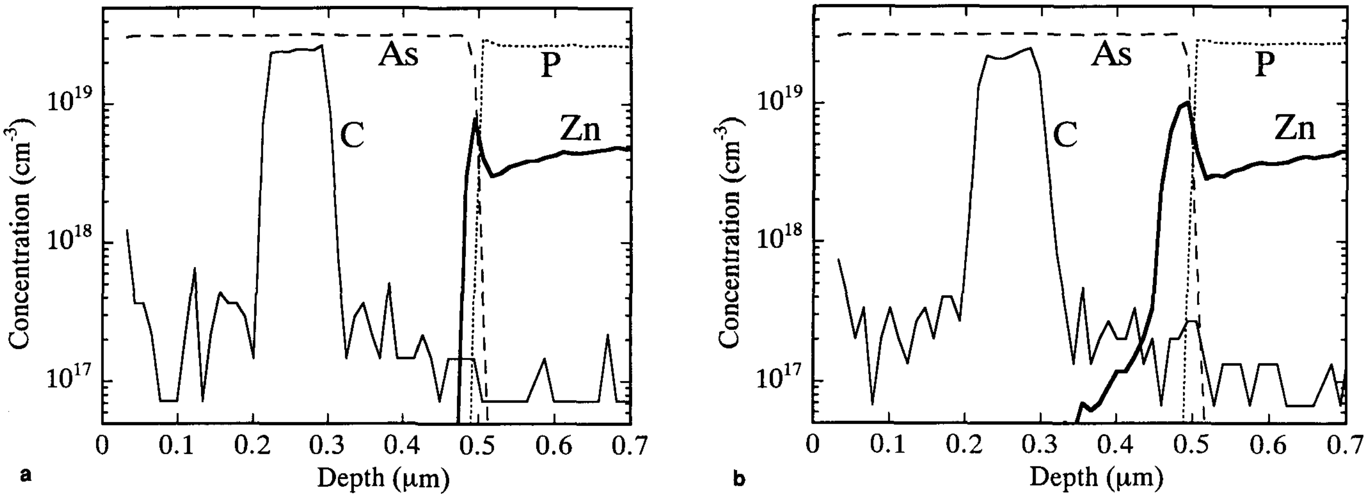

Fig. 5. (a) As-grown SIMS depth profile of a 5000Å InGaAs epitaxial layer with a 1000Å C-doping spike grown on a Zn-doped InP substrate. The As and P profiles are shown for reference. The high apparent C background (~2–3 × 10^{17} cm^{-3}) is a result of the measurement conditions, and does not represent the true C concentration in the undoped regions. (b) Depth profile after annealing the structure at ~670°C for 30 min under an AsH_3 overpressure. The Zn diffusion front has moved ~250Å further into the InGaAs epitaxial layer, while the C-doping spike has remained relatively stable.

placement of the base-emitter p-n junction is critical to the performance of the device. We have performed a preliminary evaluation of the stability of C doping profiles in InGaAs under growth-like conditions for a C doping level in excess of 2 × 10^{19} cm^{-3}.

Figure 5a shows the as-grown secondary ion mass spectrometry (SIMS) depth profile of the structure used for this study. The structure was grown on a Zn-doped InP substrate ([Zn] ~5 × 10^{18} cm^{-3}) and consists of 2000Å of undoped InGaAs (nominally n-type, n ~1 × 10^{15} cm^{-3}), followed by 1000Å of C-doped InGaAs ([C] ~2.4 × 10^{19} cm^{-3}), and capped with an additional 2000Å of undoped InGaAs (n ~1 × 10^{15} cm^{-3}). The undoped layers were grown at T_g ~625°C using TMGa, TMIn, and AsH_3, while the C-doped layer was grown at T_g ~520°C using TMIn, TEGa, AsH_3, and CCl_4. Secondary ion mass spectrometry analysis was performed using a Cameca IMS-5f instrument using a Cs^+ primary beam and positive secondary ion detection. The carbon concentration in the InGaAs was estimated by comparison with an ion-implanted (^{12}C) $In_{0.53}Ga_{0.47}As$ standard. The high apparent C background (~2–3 × 10^{17} cm^{-3}) is a result of the measurement conditions, and does not represent the true C concentration in the undoped regions.

The carbon doping spike in Fig. 5a is abrupt and appears to have suffered negligible redistribution during growth, within the resolution of the SIMS measurement. After annealing in the MOCVD reactor under typical growth-like conditions (P ~76 Torr,0.5% AsH_3 in H_2 ambient) at 670°C for 30 min, a significant amount of Zn diffusion into the InGaAs from the epilayer is evident, as shown in Fig.5b. The Zn diffusion front, defined here as the location at which the Zn concentration drops below 5 × 10^{18} cm^{-3} in the InGaAs, has shifted by 200–250Å compared to the as-grown case. The C doping spike has not widened at [C] ~5 × 10^{18} cm^{-3}, but does appear to have widened by 50–100Å at [C] ~10^{18} cm^{-3}. This may be a result of measurement error, since the resolution is limited by the amount of material sputtered between consecutive data points (~120Å in this case), or may be due to a small amount of C diffusion which could have been enhanced by the change in background doping type (n to p) in the undoped InGaAs which was caused by Zn diffusion from the substrate.[5] Although the data of Fig. 5 are preliminary and do not represent a systematic comparison of the diffusion of C and Zn in InGaAs, it is clear that abrupt C dopant profiles can be achieved by MOCVD and that the C profile is stable relative to the severe redistribution commonly observed for high Zn concentrations.

Electrical Activation of C Acceptors

We have previously described the unintentional passivation of C acceptors in InGaAs due to incorporation of hydrogen during growth and during the post-growth cool down.[18] The hydrogen passivation can be reversed by a post-growth anneal in N_2. For the present study, we have used SIMS and van der Pauw-Hall effect measurements to evaluate the activation of C acceptors in InGaAs, and have compared samples grown using TMGa and TEGa as the Ga source.

The hole concentration (measured by Hall effect, as-grown and after annealing at 440°C in N_2 for 5 min) is plotted vs the total carbon concentration ([C], determined using SIMS) for six samples in Fig. 6. All layers were approximately 5000Å thick and were cooled in the same AsH_3/H_2 ambient following growth. For the as-grown case, the hole concentration is limited to ~3 × 10^{18} cm^{-3} by H passivation. The hole concentration increases significantly upon annealing in N_2 due to reversal of the passivation (H leaves the crystal through the surface during the anneal) but remains lower than [C]. The reason for the incomplete activation of C atoms as acceptors at high doping levels is unclear at present. Carbon self-compensation (compensation of C_V acceptors by C_{III} donors) due to the amphoteric behavior of C in InGaAs is one possible explanation. Another possibility is the incorporation of nonsubstitutional C, which has been reported in heavily C-doped GaAs.[25]

All of the growth conditions for the six samples in Fig. 6 were identical, except for the Ga source, Ga source flow rate, and T_g. Three of the samples ([C] = 2.3×10^{18}, 8.7×10^{19}, and 1.8×10^{19} cm^{-3}) were grown using TMGa as the Ga source, while the other three ([C] = 1.3×10^{19}, 8.2×10^{19}, and 1.8×10^{20} cm^{-3}) were grown using TEGa. The similar degree of hydrogen passivation for similar doping levels ([C] = 1.3×10^{19} and 1.8×10^{19} cm^{-3}, for example), is a result of the fact that the final level of hydrogen passivation is established during the post-growth cool-down, and is a function of the doping level and the cooling ambient. It is also important to note that the carbon incorporation is not significantly affected by substitution of TEGa for TMGa. This serves as evidence that the source of the carbon in the InGaAs layers is the CCl_4, rather than the CH_3 radicals from the organometallic sources.

The room temperature hole mobility (μ) is plotted as a function of the hole concentration for C-doped InGaAs samples as-grown and after a post-growth anneal in N_2 in Fig. 7. All samples are 5000–7000Å thick, and were cooled in the same AsH_3/H_2 ambient following growth. The mobility decreases monotonically with increasing hole concentration among samples which have been annealed in N_2 to reverse the H passivation. This behavior is typical of heavily doped semiconductors and is a result of increased ionized impurity scattering with increasing acceptor concentration. In the as-grown case, the hole concentration saturates at ~3×10^{18} cm^{-3} as the C-doping level is increased, as described above. If the H passivation mechanism were purely a neutralization effect (formation of a neutral H-C pair), then the as-grown mobility should be a function of $P_{as\text{-}grown}$ only, and should be independent of the concentration of neutral H-C pairs. However, the as-grown mobility continues to decrease with increasing C-doping level, in spite of the fact that $p_{as\text{-}grown}$ remains constant at ~3×10^{18} cm^{-3}. These results suggest that the H-C complex which passivates the C acceptors acts as a scattering center.

For samples with $p_{annealed} < 1 \times 10^{19}$ cm^{-3}, the mobility decreases upon annealing, indicating that the H-C complex is less efficient at scattering of holes than the ionized C acceptors (C^-_{As}). For $p_{annealed} > 2 \times 10^{19}$ cm^{-3}, the hole mobility increases upon annealing. This is likely due to the fact that the conduction has become degenerate after annealing, and the effect of ionized C acceptors on scattering is reduced by degeneracy and screening effects.

Electrical Properties

The hole mobility is plotted as a function of hole concentration for a series of C-doped InGaAs layers which have been annealed to reverse the original hydrogen passivation in Fig. 8. Also included are data for Be-doped InGaAs grown by GSMBE.[26,27] The mobilities for the carbon-doped layers are comparable to those for Be-doped layers over the entire doping range studied. Thus, even for the most heavily C-doped layers, where $p_{annealed}$ ~0.4 [C], the high hole mobilities suggest low C self-compensation. In terms of majority carrier transport, C appears to be a well-behaved acceptor in $In_{0.53}Ga_{0.47}As$, as it is in GaAs, in spite of the fact that it is potentially an amphoteric dopant.

We have performed preliminary characterization of minority carrier transport in C-doped InGaAs using the zero-field time-of-flight (ZFTOF) technique. ZFTOF, which consists of measuring the transient photovoltage generated in a p^+-n diode illuminated by

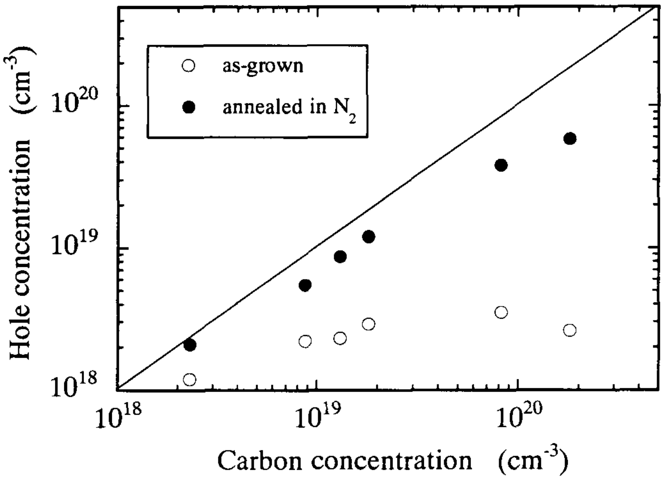

Fig. 6. Variation in hole concentration (determined by Hall effect) with total carbon concentration (determined by SIMS) for InGaAs grown on InP. The line represents the case of 100% activation of C atoms as acceptors. The as-grown hole concentration is limited by hydrogen passivation, which can be reversed by annealing at 440°C in N_2 for 5 min.

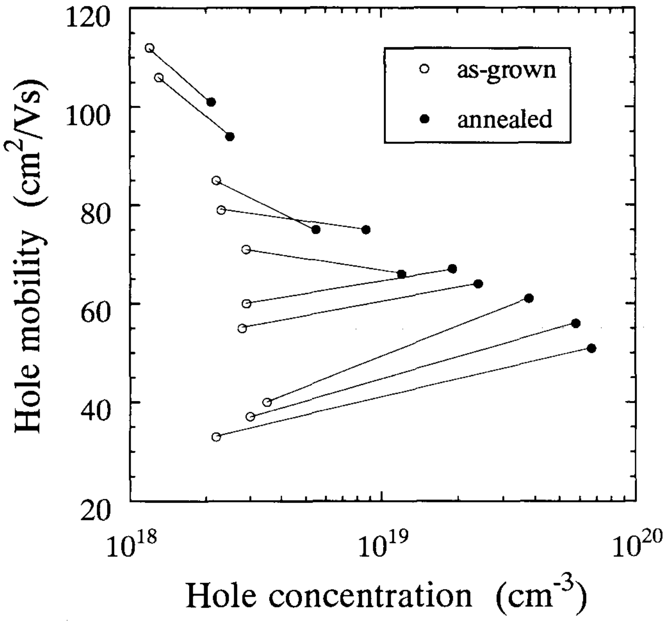

Fig. 7. 300K hole mobility as a function of hole concentration for C-doped InGaAs as-grown and after annealing in N_2 to reverse the hydrogen passivation. The lines indicate pairs of data points which correspond to the same epitaxial layer.

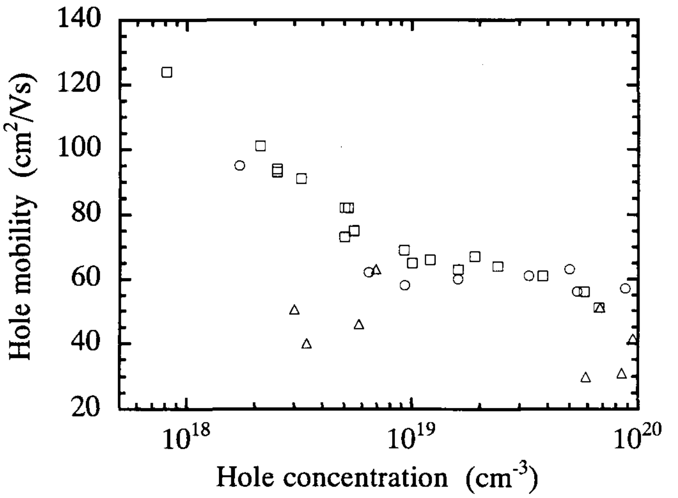

Fig. 8. Variation in hole mobility with hole concentration for C-doped InGaAs grown by MOCVD (after annealing in N_2) for this study, (□), and Be-doped InGaAs grown by GSMBE by Jackson et al., (○), and Hamm et al., (△). The mobilities are comparable over the entire doping range studied.

a picosecond light pulse at the surface of a thick p^+ layer, measures the electron transport under conditions similar to those present in an HBT and has been used to study electron transport in heavily C-doped GaAs by Colomb et al.[28] The p^+-n diodes used for these measurements were annealed in N_2 to reverse the H passivation in the 8000Å-thick p^+-InGaAs layer before fabrication of mesa diodes. Parameters adjusted to produce a fit to the transient voltage are the electron lifetime (τ_n) and diffusion coefficient (D_n). We have measured τ_n ~0.15 ns and D_n ~23 cm^2/s, which corresponds to a diffusion length of L_n ~0.6 μm, for a sample grown using TMGa as the Ga source, with $p_{annealed}$ ~1.2×10^{19} cm^{-3}. Samples grown with TEGa have also been characterized and exhibit nearly identical behavior. These preliminary results appear promising for application of C-doped InGaAs to minority carrier devices such as HBTs. Further ZFTOF studies to compare the electron transport in C and Be-doped InGaAs at higher doping levels, and to determine the effects of H passivation on electron lifetime and mobility, are currently underway.[29]

Heterojunction Bipolar Transistors

Limitations associated with the redistribution of Zn in InP/InGaAs HBT structures currently make the use of MOCVD impractical for production of high reliability HBTs. This fact has provided the motivation for the investigation of the incorporation of C in MOCVD-grown InGaAs, and the study of the electrical transport properties of the C-doped layers. We have previously reported dc results for MOCVD-grown InP/InGaAs HBTs with a C-doped base.[17] No undoped spacer layer was used at the emitter-base junction, and the low turn-on voltage for the junction indicated that displacement of the p-n junction into the emitter had not occurred. We also reported that the base doping level was limited by partial passivation of C acceptors due to incorporation of H during growth, and that the passivation could not be reversed by annealing in N_2, due to "blocking" of H outdiffusion by the emitter and collector.[18]

Recently, we have fabricated and tested microwave devices.[30] The epitaxial structure consisted of a 3000Å thick n^+-InGaAs subcollector (n ~1×10^{19} cm^{-3}), a thin n^+-InP etch stop, a 2200Å n^--InGaAs collector (n ~1×10^{15} cm^{-3}), a 1000Å thick p^+-InGaAs base ([C] ~1.5×10^{19} cm^{-3}, p ~5×10^{18} cm^{-3}), a 1000Å n-InP emitter (n ~5×10^{17} cm^{-3}), and a 1500Å-thick n^+-InGaAs contact layer (n ~2×10^{19} cm^{-3}). Devices were fabricated using an all wet chemical etching process with self-aligned base contacts (nonalloyed Ti/Pt/Au).

The maximum dc common-emitter current gain for these devices was β_{max} ~250 and showed little variation with changes in device geometry (from 60×60 μm^2 to 2×5 μm^2 emitter area). A lower limit for the electron diffusion length in the base of L_n ~1.1 μm is estimated for a current gain of 250 and base width of 1000Å, assuming unity emitter injection efficiency. This result indicates that device-quality C-doped InGaAs can be grown by MOCVD and suggests that the partial passivation of C acceptors due to incorporation of H during growth does not significantly degrade the minority carrier transport properties.

The high frequency performance was evaluated by the measurement of scattering parameters from 0 to 40 GHz. A unity current gain frequency of f_t = 62 GHz and maximum frequency of oscillation of f_{max} = 42 GHz were extrapolated from the measured data for a device with a 2×5 μm^2 emitter area. This result is comparable to the best reported results for MOCVD-grown InP/InGaAs HBTs with a Zn-doped base.[11] Further improvement in performance of devices with a C-doped base is expected for higher base doping levels. However, at the present time, the base doping levels are limited by H incorporation during growth of the device structure.

Heterojunction bipolar transistors have been grown using either TMGa or TEGa as the Ga source during growth of the C-doped base region. Device performance is similar for both cases, indicating that the minority carrier transport is not affected by the choice of the Ga source. As described above, the use of TEGa leads to improvements in base composition uniformity and run-to-run reproducibility. The use of TEGa also leads to improvements in current gain uniformity across a 2 in wafer. However, the sensitivity of device performance to small changes in substrate temperature during growth is still considered to be a major limitation associated with the use of MOCVD-grown CCl_4-doped InGaAs in HBT applications.

DISCUSSION AND CONCLUSIONS

We have demonstrated that high C incorporation can be achieved in $In_{0.53}Ga_{0.47}As$ grown by LP-MOCVD. Hole concentrations as high as ~7×10^{19} cm^{-3} have been obtained for a growth temperature of T_g ~450°C, using TEGa as the Ga source. Our results suggest that C incorporation is limited by the desorption of C-containing species from the surface during growth.

Carbon doping profiles have been shown to be stable relative to Zn under growth-like conditions. Preliminary characterization of majority and minority carrier transport indicates that C is a suitable p-type dopant for InGaAs in device applications. However, layers which are highly passivated by hydrogen suffer a reduction in hole mobility. InP/InGaAs HBTs with a C-doped base have also been demonstrated and exhibit high-frequency performance which is comparable to the best reported results for MOCVD-grown InP-based HBTs. In summary, it has been shown that C is a "well behaved" acceptor in $In_{0.53}Ga_{0.47}As$.

Although the material characterization and device results reported here are quite promising, two major difficulties associated with C-doping of InGaAs by MOCVD currently limit further progress. The first is the passivation of C acceptors by hydrogen incorporated during growth of the C-doped base region of HBT structures. It is this passivation, rather than C incorporation, which currently limits the p-type doping level in the base to less than 10^{19} cm^{-3}. Although some degree of H passivation may be inherent to MOCVD growth of C-doped InGaAs, optimization of the growth procedure (in-situ annealing or use of alternate As precursors) or device processing (ex situ annealing) may help to alleviate the problem in HBT structures.

The second limitation is the sensitivity of the alloy composition to changes in the growth conditions, especially small variations in substrate temperature. This is a result of the preferential removal of In from the surface during growth (due to etching by CCl_4), and the temperature-dependent efficiency of the organometallic Ga sources at low temperatures. The substitution of TMGa with TEGa has resulted in measurable improvement in run-to-run reproducibility and in uniformity. However, the temperature dependence of the alloy composition is still severe and can cause measurable variation in device performance across a 2 in wafer. This issue may be best addressed through the use of alternate carbon dopant sources which do not result in etching and the use of organometallic Ga sources with lower thermal stability than TEGa.

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REFERENCES

1. B.T. Cunningham, M.A. Haase, M.J. McCollum, J.E. Baker and G.E. Stillman, *Appl. Phys Lett.* 54, 1905 (1989).
2. N.I. Buchan, T.F. Kuech, G. Scilla and F. Cardone, *J. Cryst. Growth* 110, 405 (1991).
3. A. E. Kibbler, S.R. Kurtz and J.M. Olson, *J. Cryst. Growth* 109, 258 (1991).
4. T.F. Kuech, M.A. Tischler, P.J. Wang, G. Scilla, R. Potemski and F. Cardone, *Appl. Phys. Lett.* 53, 1317 (1988).
5. B.T. Cunningham, L.J. Guido, J.E. Baker, J.S. Major, Jr., N. Holonyak, Jr. and G.E. Stillman, *Appl. Phys. Lett.* 55, 687 (1989).
6. B.T. Cunningham, G.E. Stillman and G.S. Jackson, *Appl. Phys Lett.* 56, 361 (1990).
7. F. Ren, T.R. Fullowan, J. Lothian, P.W. Wisk, C.R. Abernathy, R.F. Kopf, A.B. Emmerson, S.W. Downey and S.J. Pearton, *Appl. Phys. Lett.* 59, 3613 (1991).
8. Y.K. Chen, R.N. Nottenburg, M.B. Panish, R.A. Hamm and D.A. Humphrey, *IEEE Electron Dev. Lett.* 10, 267 (1989).
9. W.E. Stanchina, J.F. Jensen, R.A. Metzger, M.E. Hafizi and D.B. Rensch, *Proc. 4th Int. Conf. on InP*, April 1992, p. 434.
10. R. Bhat, J.R. Hayes, H. Schumacher, M.A. Koza, D.M. Hwang and M.H. Meynadier, *J. Cryst. Growth* 93, 919 (1988).
11. R.N. Nottenburg, Y.K. Chen, T. Tanbun-Ek, R.A. Logan and D.A. Humphrey, *Appl. Phys. Lett.* 55, 171 (1989).
12. C.R. Abernathy, S.J. Pearton, F. Ren, W.S. Hobson, T.R. Fullowan, A. Katz, A.S. Jordan and J. Kovalchick, *J. Cryst. Growth* 105, 375 (1990).
13. H. Ito and T. Ishibashi, *Jpn. J. Appl. Phys.* 30, L944 (1991).
14. T.P. Chin, P.D. Kirchner, J.M. Woodall and C.W. Tu, *Appl. Phys. Lett.* 59, 2865 (1991).
15. R.C. Gee, T.P. Chin, C.W. Tu, P.M. Asbeck, C.L. Lin, P.D. Kirchner and J.M. Woodall, *IEEE Electron Dev. Lett.* 13, 247 (1992).
16. S.A. Stockman, A.W. Hanson and G.E. Stillman, *Appl. Phys. Lett.* 60, 2903 (1992).
17. A.W. Hanson, S.A. Stockman and G.E. Stillman, *IEEE Electron Dev. Lett.* 13, 504 (1992).
18. S.A. Stockman, A.W. Hanson, S.M. Lichtenthal, M.T. Fresina, G.E. Höfler, K.C. Hsieh and G.E. Stillman, *J. Electron. Mater.* 21, 1111 (1992).
19. M.C. Hanna, Z.H. Lu and A. Majerfeld, *Appl. Phys. Lett.* 58, 164 (1991).
20. C. Plass, H. Heinecke, O. Kayser, H. Lüth and P. Balk, *J. Cryst. Growth* 88, 455 (1988).
21. S.J.W. Price, *Comprehensive Chemical Kinetics*, ed. C.H. Bamford and C.F.H. Tipper (New York: Elsevier, 1972), vol. 4, p. 197.
22. B.T. Cunningham, J.E. Baker and G.E. Stillman, *Appl. Phys. Lett.* 56, 836 (1990).
23. B.T. Cunningham, J.E. Baker, S.A. Stockman and G.E. Stillman, *Appl. Phys. Lett.* 56, 1760 (1990).
24. P. Enquist, *J. Appl. Phys.* 71, 704 (1992).
25. G.E. Höfler and K.C. Hsieh, *Appl. Phys. Lett.* 61, 327 (1992).
26. R.A. Hamm, M.B. Panish, R.N. Nottenburg, Y.K. Chen and D.A. Humphrey, *Appl. Phys. Lett.* 54, 2586 (1989).
27. S.L. Jackson and G.E. Stillman (unpublished data).
28. C.M. Colomb, S.A. Stockman, N.F. Gardner, A.P. Curtis, G.E. Stillman, T.S. Low, D.E. Mars and D.B. Davito, *J. Appl. Phys.* 73, 7471 (1993).
29. C.M. Colomb, S.A. Stockman, S.L. Jackson, N.F. Gardner, S. Varadarajan, A.W. Hanson, M.T. Fresina, A.P. Curtis and G.E. Stillman (to be published).
30. A.W. Hanson, M.T. Fresina, S.A. Stockman, S.T. Uribe and G.E. Stillman (to be published).