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Passivation of Carbon Acceptors during Growth of Carbon-Doped GaAs, InGaAs, and HBTs by MOCVD

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Carbon doped *p*-type GaAs and $In_{0.53}Ga_{0.47}As$ epitaxial layers have been grown by low-pressure metalorganic chemical vapor deposition using CCl_4 as the carbon source. Low-temperature post-growth annealing resulted in a significant increase in the hole concentration for both GaAs and $In_{0.53}Ga_{0.47}As$, especially at high doping levels. The most heavily doped GaAs sample had a hole concentration of 3.6×10^{20} cm^{-3} after a 5 minute anneal at ~400° C in N_2, while the hole concentration in $In_{0.53}Ga_{0.47}As$ reached 1.6×10^{19} cm^{-3} after annealing. This annealing behavior is attributed to hydrogen passivation of carbon acceptors. Post-growth cool-down in an AsH_3/H_2 ambient was found to be the most important factor affecting the degree of passivation for single, uncapped GaAs layers. No evidence of passivation is observed in the base region of InGaP/GaAs HBTs grown at ~625° C. The effect of *n*-type cap layers and cool-down sequence on passivation of C-doped InGaAs grown at ~525° C shows that hydrogen can come from AsH_3, PH_3, or H_2, and can be incorporated during growth and during the post-growth cool-down. In the case of InP/InGaAs HBTs, significant passivation was found to occur in the C-doped base region.

Key words: Hydrogen passivation, carbon doping, metalorganic chemical vapor deposition (MOCVD), heterojunction bipolar transistors (HBTs)

I. INTRODUCTION

Low-resistivity, *p*-type GaAs and InGaAs are of interest for the base region of *n-p-n* heterojunction bipolar transistors (HBTs), where the high-frequency performance is dependent on the external base resistance.[1] Heavily carbon doped *p*-type GaAs has been achieved by several growth techniques, including metalorganic molecular beam epitaxy (MOMBE),[2] molecular beam epitaxy (MBE),[3] and metalorganic chemical vapor deposition (MOCVD).[4] Carbon has been used as the base dopant in AlGaAs/GaAs HBTs,[3,5] and has an advantage over other *p*-type dopants due to its relatively low diffusion coefficient in GaAs.[6,7] The use of carbon as a *p*-type dopant for InGaAs may also be attractive for use in InP/InGaAs HBTs if the atomic diffusion coefficient is also low in this material. Carbon doping of InGaAs has been investigated recently for growth by MBE-based techniques[8–10] and by MOCVD.[11]

Hydrogen incorporation in III-V materials has been shown to occur under a wide variety of conditions, and can result in reversible passivation of donors and acceptors.[12–15] It has also been shown that among acceptors in GaAs, C is most efficiently passivated by hydrogen.[16] Intentional hydrogen passivation of carbon acceptors in GaAs and AlGaAs has been demonstrated, and has even been used as a technique for lateral definition of stripe geometry laser diodes.[17,18] The presence of hydrogen-carbon bonds in C-doped GaAs grown by MOMBE has been detected by infrared absorption analysis,[19] indicating that unintentional passivation can occur during growth.

Several groups have reported unintentional hydrogen passivation in CCl_4-doped GaAs and AlGaAs grown by MOCVD. Höfler *et al.*[20] observed an increase in the hole concentration (from 2.5×10^{19} to 4.0×10^{19} cm^{-3}) in C-doped GaAs upon annealing in a sealed ampoule at 825° C, and also detected a high hydrogen concentration in as-grown GaAs and AlGaAs using SIMS. Watanabe and Yamazaki[21] observed similar annealing behavior in C-doped AlGaAs. A recent study by Hobson and coworkers[22] showed that up to 6×10^{19} cm^{-3} carbon acceptors may be passivated by hydrogen in CCl_4-doped GaAs grown by MOCVD using AsH_3 or TBAs as the arsenic source. This passivation was reversed by an anneal at 550° C in a He environment, and the hole concentration was found to increase by as much as 50 to 100% after annealing.

Antell *et al.*[23] have found that Zn acceptors in MOCVD-grown InP may be passivated when the InP is capped with *p*-type InGaAs. They showed that hydrogen generated from pyrolysis of AsH_3 became trapped in the InP during the post-growth cool-down, and was responsible for the acceptor passivation. Cole and coworkers[24] reported similar findings for cooling of Zn- and Cd-doped InP in an AsH_3-containing ambient, and also showed that the presence of PH_3 could result in measurable passivation.

Chin *et al.*[10] have grown *p*-type C-doped InGaAs by gas source molecular beam epitaxy (GSMBE) using CCl_4 as the carbon source and AsH_3, elemental In, and elemental Ga as the growth precursors. They found that the hole concentration for samples grown

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at 420° to 460° C could be increased by a factor of ten by a post-growth anneal at 420° C in N_2. Similar behavior has been observed for C-doped InGaAs grown by MOCVD.[11] In addition, two reports of InP/InGaAs HBTs with a carbon-doped base suggest that the hole concentration in the base may be reduced by hydrogen passivation.[25,26]

In this paper, we use low-temperature post-growth annealing and Hall effect measurements to investigate the hydrogen passivation of carbon in GaAs and InGaAs during MOCVD growth and post-growth cool-down. InGaP/GaAs and InP/InGaAs HBTs with a carbon doped base were also subjected to post-growth anneals, and the effect on the base region is discussed. It is also demonstrated that the presence of AsH_3, PH_3, or H_2 in the cooling ambient may lead to passivation in heavily C-doped layers.

II. EXPERIMENTAL

All growths for this study were carried out in a modified Emcore GS3100 low-pressure MOCVD reactor at 76 Torr. The growth precursors were TMIn, TMGa, AsH_3, and PH_3. CCl_4 was used as the p-type dopant, and SiH_4 and Si_2H_6 were used as the n-type dopant sources. All GaAs layers were grown on semi-insulating (100) GaAs substrates misoriented 2° toward (110). Relatively low growth temperatures were used ($T \leq 625°$ C) in order to achieve high carbon doping levels for the single layers of GaAs. Carbon incorporation was also controlled by varying the CCl_4 flow rate and the V/III ratio. The InGaP/GaAs HBT structures were grown at ~625° C, and consisted of a 5000Å n^+-GaAs subcollector ($n \sim 1 \times 10^{19}$ cm^{-3}), 5000Å n^--GaAs collector ($n \sim 4 \times 10^{16}$ cm^{-3}), 730Å p^+-GaAs base ($p \sim 2.5 \times 10^{19}$ cm^{-3}), 1500Å n-$In_{0.5}Ga_{0.5}P$ emitter ($n \sim 1 \times 10^{18}$ cm^{-3}), and 1500Å n^+-GaAs/InGaAs contact layer ($n \sim 1 \times 10^{19}$ cm^{-3}). An AsH_3 overpressure was maintained following the growth of single layers and HBT structures until the substrate temperature fell to approximately 250° C.

All InGaAs layers were grown on semi-insulating (100) InP substrates misoriented 2° toward (110). Low growth temperatures (~525° C) and low V/III ratios were employed in order to obtain high p-type doping in $In_{0.53}Ga_{0.47}As$. The alloy composition is strongly affected by the presence of CCl_4 during growth,[11,27] so the TMGa/TMIn ratio must be adjusted to maintain lattice match to InP. The InP/InGaAs HBT structures consisted of a 5000Å n^+-InP subcollector ($n \sim 1 \times 10^{19}$ cm^{-3}), a 5000Å n^--InGaAs collector ($n \sim 1 \times 10^{15}$ cm^{-3}), a 1000Å p^+-InGaAs base ($p \sim 1.2 \times 10^{19}$ cm^{-3}), a 1500Å n-InP emitter ($n \sim 1 \times 10^{18}$ cm^{-3}), and a 1000Å n^+-InGaAs contact layer ($n \sim 1 \times 10^{19}$ cm^{-3}). An AsH_3 overpressure was also maintained in this case until the temperature had decreased to about 250° C after growth of InGaAs layers and HBTs, except where noted otherwise.

The room temperature carrier concentration and mobility were determined by van der Pauw-Hall measurements on 6 mm × 6 mm samples with non-alloyed indium ohmic contacts at the sample corners. Transmission line measurement (TLM) patterns were used to measure the sheet resistance of the base region in the HBT structures. The thickness of the epitaxial layers was determined by scanning electron microscopy (SEM) or surface profilometry measurement of selectively etched samples. Secondary ion mass spectrometry (SIMS) measurements were performed on several GaAs layers to estimate the total carbon concentration, using a carbon-implanted GaAs substrate as a calibration standard. The post-growth anneals were performed in an alloying station, with the samples placed directly upon a resistively heated graphite strip. All anneals were 5 minutes in duration, and were performed in a 100% N_2 atmosphere.

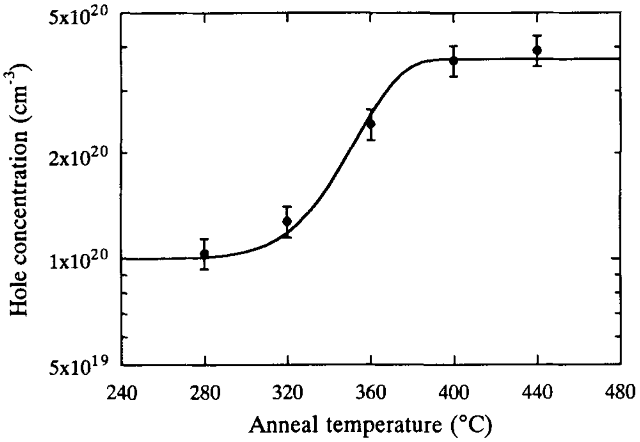

Fig. 1 — Variation of the hole concentration with anneal temperature for a 0.25 μm thick, heavily C-doped GaAs epitaxial layer. Anneals were 5 min in duration, and were performed in a 100% N_2 ambient.

III. RESULTS

A. Carbon-doped GaAs

The dependence of hole concentration on post-growth annealing temperature for one of the most heavily doped GaAs layers is shown in Figure 1. Each data point represents an individual Hall sample, which was annealed before making ohmic contacts. For anneal temperatures of less than 320° C, the hole concentration remained essentially constant near 1.0 × 10^{20} cm^{-3}. However, a hole concentration of 3.6 × 10^{20} cm^{-3} was measured after annealing at 400° C for 5 minutes in N_2. Thus, the fraction of carbon acceptors initially passivated was [HC]/[C] ~ $(p_{\text{annealed}} - p_{\text{as-grown}})/(p_{\text{annealed}}) = 0.7$, where [HC] is the concentration of carbon acceptors passivated by hydrogen, and [C] is the total carbon concentration, which is assumed to be equal to the hole concentration after the passivation has been reversed (p_{annealed}), as discussed below. The hole mobility decreased from 64 cm^2/Vs in the as-grown sample to 51 cm^2/Vs after annealing at 400° C. This change is consistent with the increase in the hole concentration.

The total carbon concentration for this sample was estimated from SIMS measurements to be [C] ~ 2.5 × 10^{20} cm^{-3}. This is lower than the hole concentration measured by Hall effect, but is in agreement within the experimental error inherent in the SIMS technique, suggesting near unity electrical activation of C atoms as acceptors. Similar results have been found for other heavily doped ([C] > 5 × 10^{19} cm^{-3}) GaAs layers. SIMS analysis also showed a high hydrogen level in the C-doped GaAs layers, but the hydrogen concentration was not measured quantitatively.

The heavily C-doped GaAs epitaxial layers exhibit a significant degree of lattice contraction, due to the small covalent bonding radius of C (0.77Å) relative to Ga (1.26Å) and As (1.20Å). For the sample described in Fig. 1, the mismatch changed from $\Delta a/a = -2.9 \times 10^{-3}$ before annealing to $\Delta a/a = -4.5 \times 10^{-3}$ after annealing at 400° C. This change can be explained by removal of hydrogen, assuming that the effective bonding radius of a carbon-hydrogen pair is larger than for carbon alone. The mismatch after annealing is in good agreement with Vegard's law, which predicts a lattice contraction of $\Delta a/a = -4.5 \times 10^{-3}$ for $[C]_{As} = 3 \times 10^{20}$ cm^{-3} for a coherently strained epitaxial layer.

The dependence of hydrogen incorporation on growth conditions was explored by comparing the hole concentration in the as-grown samples to that measured after reversing the passivation by annealing, and it was found that the fraction of C acceptors passivated always increased for conditions which favored high carbon incorporation. In Fig. 2, the fraction of C acceptors passivated ([HC]/[C]) is shown as a function of total carbon concentration for as-grown GaAs layers grown at temperatures ranging from 575 to 625° C and with V/III ratios between 3 and 50. The fraction of carbon acceptors passivated was found to be correlated with the carbon concentration, with [HC]/[C] highest for high doping levels.

The ohmic contacts were removed from these GaAs layers after they had been annealed to reverse the passivation. The samples were then placed in the MOCVD system and heated to 500° C in an AsH_3/H_2 ambient, maintained at that temperature for 2.5 minutes, then cooled to 250° C. The molar fraction of AsH_3 in the ambient was $[AsH_3] = 10^{-3}$. The AsH_3 flow was stopped at 250° C, and the samples were further cooled to room temperature in H_2. This sequence was chosen in order to simulate the cool-down which occurs immediately after growth, although a higher AsH_3 mole fraction was present during the original post-growth cool-down for several of the samples. Non-alloyed Hall contacts were then made to the samples, and it was found that the hole concentration had returned to nearly the same value measured immediately after growth, *i.e.* nearly the same fraction of C acceptors were passivated for each of the samples as had been passivated after growth, as shown in Fig. 2.

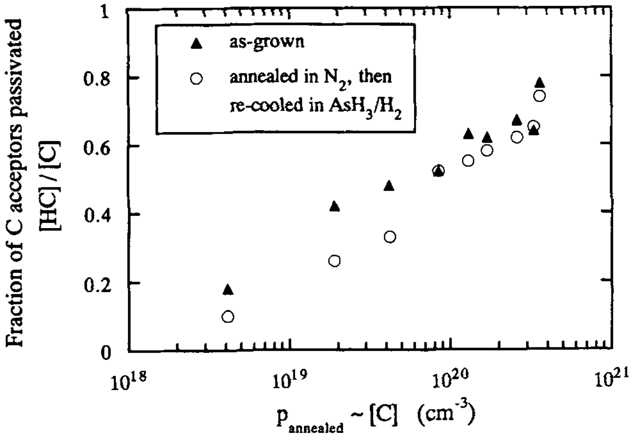

Fig. 2 — Fraction of carbon acceptors passivated by hydrogen as a function of total carbon concentration for several heavily doped GaAs samples. The layers are all between 2500 and 5000Å thick. The total carbon concentration, [C], has been assumed to be equal to the hole concentration after annealing at 400° C in N_2 for 5 minutes. The (▲) represent the fraction of acceptors passivated immediately after growth, while the (○) represent the fraction of acceptors passivated after annealing the sample in N_2 to reverse the passivation, then heating to 500° C and re-cooling in an AsH_3/H_2 mixture where the AsH_3 mole fraction was $[AsH_3] = 1 \times 10^{-3}$.

These results show that the post-growth cool-down is very important in determining the amount of hydrogen passivation in a heavily doped GaAs layer when the surface is exposed to a AsH_3/H_2 ambient. Thus, heavily-doped *p*-type contact layers at the surface of a device structure may be especially susceptible to unintentional hydrogen passivation during post-growth cool-down. The amount of passivation measured in these layers for a given [C] is determined primarily by the cool-down, so we are unable to draw any conclusions regarding incorporation of hydrogen during growth using this data.

Several of these layers were also heated to 500° C and cooled in a 100% H_2 ambient after annealing in N_2 to reverse the original passivation. Hall effect measurements give [HC]/[C] ~ <0.1 for the most heavily doped samples. Thus, the amount of AsH_3 present during cool-down is an important factor in determining the amount of passivation. In fact, the three most lightly doped samples in Fig. 2 were originally cooled with $[AsH_3] = 2.5 \times 10^{-3}$ to 5×10^{-3} after growth, and all three exhibited a slightly higher degree of passivation after growth than after heating and cooling with $[AsH_3] = 1 \times 10^{-3}$.

Several samples from the epitaxial layer described in Fig. 1 were annealed at ~400° C in N_2 to reverse the original passivation, then heated to different temperatures and cooled in the AsH_3/H_2 ambient. It was found that heating to 450 or 500° C produced nearly the same result ([HC]/[C] ~ 0.7). However, when the sample was heated to ~400° C for 2.5 minutes and then cooled, the fraction of acceptors passivated was only [HC]/[C] ~ 0.5. This indicates that the hydrogen is likely trapped within the GaAs during cool-down when the sample temperature is around 400 to 450° C.

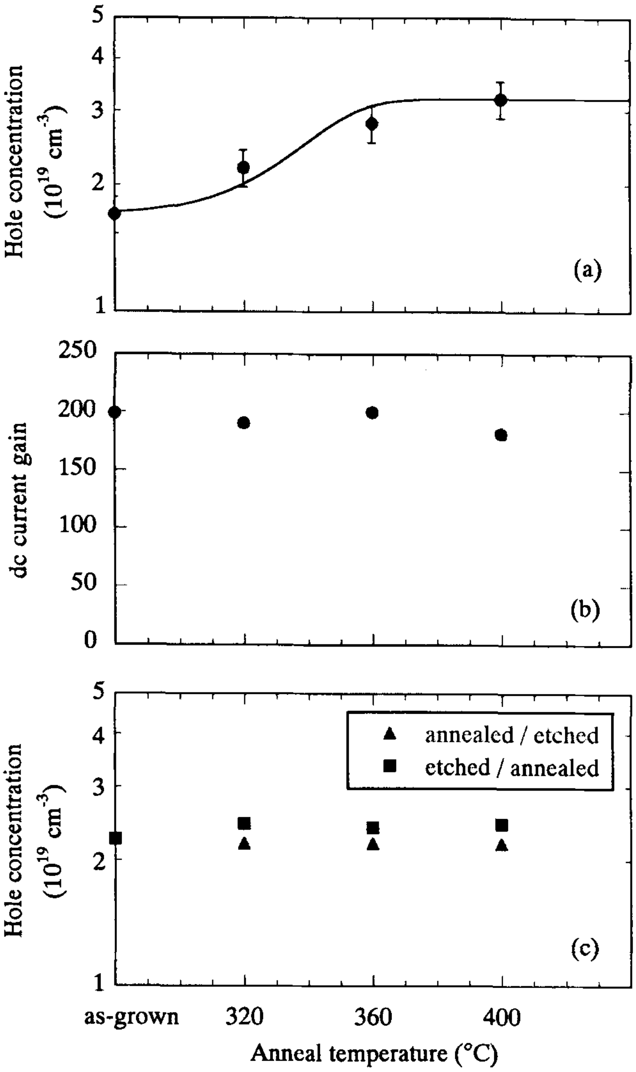

Fig. 3 — (a) Hole concentration versus anneal temperature for a 2200Å thick C-doped GaAs layer. This sample was the base doping calibration layer for the HBTs. (b) Variation in dc current gain with anneal temperature for InGaP/GaAs HBTs with a C-doped base. The anneals were performed prior to device fabrication. (c) Hole concentration in the base layer as a function of anneal temperature for two cases: (▲) represents the case where the anneals were performed before removing the emitter, and (■) represents the case where the emitter was removed prior to annealing in N_2. All anneals were performed in a 100% N_2 ambient for 5 minutes.

B. *InGaP/GaAs HBTs*

We have investigated the effect of hydrogen passivation on the base region of $In_{0.5}Ga_{0.5}P$/GaAs HBTs with a carbon-doped base. The annealing behavior of the base doping calibration layer is shown in Fig. 3(a). The doping calibration layer is simply a single C-doped GaAs layer grown on a semi-insulating GaAs substrate. Anneals were 5 minutes in duration and were performed in N_2. The hole concentration increased from 1.7×10^{19} cm^{-3} to 3.2×10^{19} cm^{-3} upon annealing at 400° C, indicating that the fraction of C acceptors initially passivated by hydrogen was ~0.47.

The base region of the HBT structure was grown under the same conditions as the doping calibration layer. The dc characteristics of these HBTs were measured after post-growth annealing at 320, 360, and 400° C. The anneals were performed prior to any device processing. The device fabrication was carried out using selective wet chemical etching techniques, and Ti/Pt/Au contacts (sintered at ~260° C) were employed in order to avoid high-temperature processing steps. The emitter area was 60 μm × 60 μm, and a collector current of 10mA was used to measure the dc common-emitter current gain, β. The dc current gain of the HBTs might be expected to decrease significantly after annealing, since β should be inversely proportional to the hole concentration in the base region.[1] However, no significant changes were observed in the device characteristics after annealing. For example, the dc current gain decreased by less than 10% upon annealing at 400° C, as can be seen in Fig. 3(b).

In order to determine more directly whether H passivation affected the base region of these structures, Hall effect measurements were used to measure the hole concentration in the base for two sets of annealed HBT structures. The depletion region between the p^+ base and the n-type collector served to isolate the base from the conducting regions below. For the first set, samples were annealed before etching the emitter away from the structure, and Hall measurements were performed using non-alloyed In contacts. For the second set, the samples were annealed after etching the emitter to remove the base-emitter p-n junction, which might play a role in trapping ionized hydrogen in the base (hydrogen is expected to diffuse as a proton, H^+, in p-type GaAs[28]), and Hall measurements were also performed. The hole concentration as a function of anneal temperature is given in Fig. 3(c). No significant changes were observed in either case—the hole concentration stayed essentially unchanged at the value measured in the base of a structure which was not annealed. The discrepancy between the hole concentration measured for the 730Å base ($p \sim 2.5 \times 10^{19}$ cm^{-3}) and the 2200Å doping calibration layer after annealing ($p \sim 3.2 \times 10^{19}$ cm^{-3}) is likely due to uncertainty in the surface and interface depletion corrections used for these very thin layers. The base sheet resistance was also measured using TLM patterns for an as-grown structure (not annealed), and for structures where annealing at 400° C was performed before or after removal of the emitter, as described above. The sheet resistance was essentially unchanged at 520 ± 25 Ω/sq. for all three cases, in agreement with the Hall effect results.

The results described above show that very little passivation ($[HC]/[C] < 0.05$) occurred in the base region of the HBT structure, even though ~47% of C acceptors were passivated in the single C-doped GaAs layer used for doping calibration which was grown under identical conditions. A likely explanation is that hydrogen is unable to penetrate the n-type InGaP emitter during post-growth cool-down, since we have shown that the cool-down in an AsH_3/H_2 ambient determines the amount of passivation in C-doped GaAs layers whose surface is exposed during cool-down. The results described for the HBT seem to imply that very little hydrogen passivation occurs during growth at 625° C, and that passivation may not occur in the buried base layer during post-growth cool-down.

Another possible explanation for this behavior is that hydrogen incorporated during growth of the base can diffuse out of the sample during growth of the InGaP emitter due to the replacement of AsH_3 with PH_3 in the growth ambient. It has been shown that Zn acceptors in InP may be more highly passivated by hydrogen generated from pyrolysis of AsH_3 than from PH_3.[24] Thus in our case, removal of AsH_3 from the growth ambient could result in a lower concentration of atomic hydrogen at the surface during growth, and a net out-diffusion of hydrogen from the C-doped GaAs during initial stages of growth of the emitter.

C. Carbon-doped InGaAs

We have also investigated the effect of hydrogen passivation on C-doped $In_{0.53}Ga_{0.47}As$. The major difference between growth of C-doped InGaAs and GaAs is that lower growth temperatures are required to achieve high carbon incorporation in InGaAs. The fraction of C acceptors passivated is shown as a function of the hole concentration after annealing ($p_{annealed}$) in Fig. 4. The passivation was reversed by annealing at 400° C for 5 minutes in N_2, and the fraction of acceptors passivated was determined by comparing the hole concentration before and after annealing, as described above for C-doped GaAs. SIMS has been used to confirm the presence of carbon and hydrogen in these layers, but the concentrations of C and H have not yet been quantified by comparison with appropriate calibration standards.

The effect of re-cooling these C-doped InGaAs layers in the same ambient used during the original post-growth cool-down was also studied. Samples were first annealed at 400° C in N_2 to reverse the original passivation. They were then heated to 500° C, held at that temperature for 2.5 minutes, cooled to 250° C in AsH_3/H_2 ($[AsH_3] = 3 \times 10^{-4}$), and then cooled the rest of the way to room temperature in H_2, as described earlier for GaAs. Ohmic contacts were then made, and Hall measurements were performed. As in the case of C-doped GaAs, we found that the fraction of C acceptors passivated returned to nearly the same value as that measured immediately after growth, as shown in Fig. 4.

The trend of increasing degree of passivation with increasing doping level shown in Fig. 4 is similar to the trend we have observed for GaAs. However, the C-doped InGaAs layers are much more highly passivated than GaAs layers for comparable doping levels and thicknesses. For example, an $In_{0.53}Ga_{0.47}As$ layer with $p_{annealed} \sim 1 \times 10^{19}$ cm^{-3} is ~80% passivated immediately after growth, while a GaAs layer with $p_{annealed} \sim 1 \times 10^{19}$ cm^{-3} is ~20–30% passivated. These values are dependent on the cool-down ambient, but the difference between GaAs and InGaAs is significant. In fact, we have found that for $In_xGa_{1-x}As$ where $x \sim 0.7$, n-type conduction is observed after growth, but the layers become strongly p-type ($p > 5 \times 10^{17}$ cm^{-3}) after annealing in N_2.

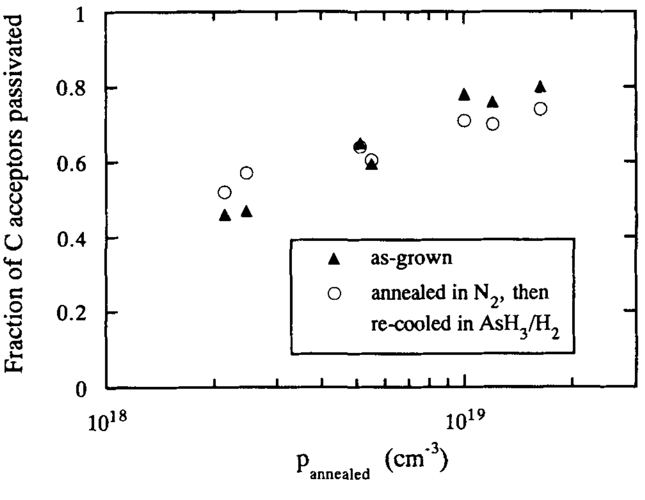

Fig. 4 — Fraction of carbon acceptors passivated by hydrogen as a function of hole concentration after annealing for several C-doped $In_{0.53}Ga_{0.47}As$ samples. The layers are all between 5000 and 8000Å thick. The (▲) represent the fraction of acceptors passivated immediately after growth, while the (○) represent the fraction of acceptors passivated after annealing the sample in N_2 to reverse the passivation, then heating to 500° C and re-cooling in an AsH_3/H_2 mixture where the AsH_3 mole fraction was $[AsH_3] = 3 \times 10^{-4}$.

Single $In_{0.53}Ga_{0.47}As$ layers were grown on InP substrates at 525° C, and cooled under different ambients (AsH_3/H_2, PH_3/H_2, or 100% H_2) to investigate the effect of cool-down on thin (~1000Å) layers. All of the samples were grown under identical conditions, and the hole concentration for each of these layers was measured to be 1.2×10^{19} cm^{-3} after annealing at 400° C in N_2. The as-grown hole concentration for samples cooled in varying AsH_3/H_2 and PH_3/H_2 mixtures is shown in Fig. 5. AsH_3 was found to produce more highly passivated layers

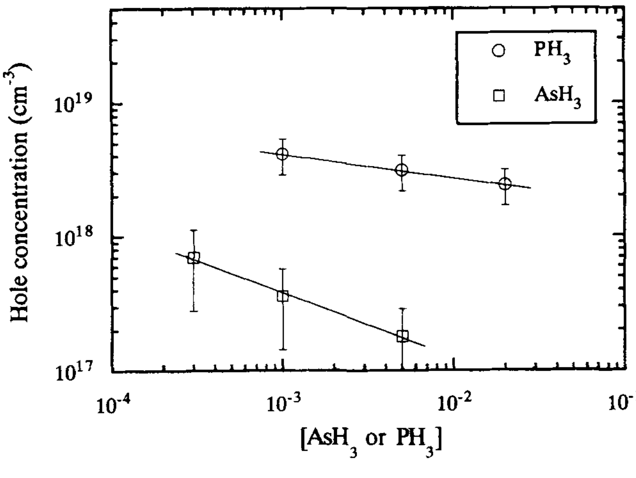

Fig. 5 — Hole concentration measured for thin (1000Å) C-doped epitaxial layers as a function of the mole fraction of AsH_3 of PH_3 present in an AsH_3/H_2 or PH_3/H_2 ambient during post-growth cool-down. The hole concentration for all of these samples is $\sim 1.2 \times 10^{19}$ cm^{-3} after annealing at 400° C in N_2 for 5 minutes.

than PH_3, as demonstrated by the lower as-grown hole concentration for samples cooled in AsH_3/H_2. This is likely due to the fact that the As-H bond in AsH_3 is weaker than the P-H bond in PH_3, so more efficient pyrolysis of AsH_3 should result in more atomic hydrogen becoming available at the surface during cool-down. The data also show that the amount of AsH_3 or PH_3 present during cool-down can affect the degree of passivation. One sample was cooled in a 100% H_2 ambient after growth, and the as-grown hole concentration measured 8.4×10^{18} cm^{-3}, suggesting that hydrogen passivation of C-doped InGaAs can occur in the absence of AsH_3 or PH_3 during cool-down. We also note that the fraction of C acceptors passivated is slightly higher for a 1000Å-thick InGaAs layer (~0.94) than for an 8000Å-thick layer (~0.76) grown under the same conditions and cooled in the same ambient (AsH_3/H_2, with $[AsH_3] \sim 3 \times 10^{-4}$).

Several of the samples described above were placed back in the MOCVD reactor, heated to 500° C, and cooled in the same ambient which was present during the original post-growth cool-down. In each case, the sample was divided into two pieces—one which had been annealed in N_2 to reverse the original passivation, (a), and one which was left in the passivated state, (b). The results are given in Table I. Sample #420, for example, was originally cooled in an AsH_3/H_2 ambient. Both pieces of the sample (420a and 420b) were measured to have the same hole concentration ($p \sim 2 \times 10^{17}$ cm^{-3}) after being re-cooled in the same ambient as was measured after growth. This shows that the degree of passivation is determined by the cool-down—the original state of passivation was restored in sample 420a, even though the hydrogen passivation which had occurred during the post-growth cool-down had already been reversed. It can also be seen that no further decrease in hole concentration was observed in sample 420b after re-cooling in the same ambient. The original state of passivation was maintained in sample 420b, so there was no net change in the number of C acceptors passivated. Similar results can be seen for samples cooled in PH_3/H_2 or H_2 only. The fact that sample 422a was re-passivated by re-cooling in H_2 demonstrates that passivation can occur as a result of cooling in H_2 only.

D. InP/InGaAs HBTs

We have also investigated the passivation behavior in InP/InGaAs HBTs with a carbon-doped base. The dc performance of these devices has been reported elsewhere,[26] and the discussion here will be limited to the passivation behavior. The base region was grown under the same conditions as the 1000Å thick layers described in the previous section. The rest of the device structure was grown at 625° C. TLM patterns were employed to measure the base sheet resistance for these structures. Hall effect measurements on the base region proved to be unreliable due to parallel conduction in the collector and subcollector, so in order to examine the behavior in the base region by Hall effect, a pseudo-HBT structure, in which the collector and subcollector were left out, was grown on a semi-insulating InP substrate. Hall measurements were performed on this structure after removal of both the emitter cap and emitter using selective etching.

The effect of hydrogen passivation on the base region is summarized in Table II. The as-grown hole concentration for an 8000Å thick base doping calibration layer was 3×10^{18} cm^{-3}. After annealing at 400° C in N_2, the hole concentration increased to 1.2×10^{19} cm^{-3}. The base sheet resistance was measured for three cases. In the first case, the emitter was removed and no anneal was performed, and a sheet resistance of 1350 Ω/sq was measured. This corresponds to an estimated hole concentration of $\sim 7 \times 10^{18}$ cm^{-3}. In the second case, the sample was annealed after removing the emitter, but before evaporation of the Ti/Pt/Au contacts. The sheet resistance measured 800 Ω/sq, indicating nearly complete reversal of the passivation. In the last case, the sample was annealed before etching off the emitter, and the base sheet resistance was 1620 Ω/sq. Thus, the passivation was not reversed in the case where the n-type emitter structure was left intact during the anneal. The results of Hall effect measurements on the pseudo-HBT structure are also shown in Table II. The reason for the slight increase in the passivation for the case where the emitter is removed after annealing is not clear at present. The hole concentration in thin InGaAs layers is not affected by submerging in the etch used to remove the

Table I. The effect of various cooling ambients on the hole concentration in 1000Å-thick C-doped $In_{0.53}Ga_{0.47}As$ layers. All samples exhibit a hole concentration of 1.2×10^{19} cm^{-3} after annealing at 400° C in N_2 for 5 minutes.

Sample #	Post-Growth Cool-Down Ambient	As-Grown Hole Concentration (10^{18} cm^{-3})	Annealed in N_2?	p After Re-Cooling in Same Ambient (10^{18} cm^{-3})
420a	AsH_3/H_2, $[AsH_3] \sim 5 \times 10^{-3}$	~0.2	Y	~0.2
420b	AsH_3/H_2, $[AsH_3] \sim 5 \times 10^{-3}$	~0.2	N	~0.2
421a	PH_3/H_2, $[PH_3] \sim 2 \times 10^{-2}$	2.4	Y	3.3
421b	PH_3/H_2, $[PH_3] \sim 2 \times 10^{-2}$	2.4	N	3.2
422a	100% H_2	9.5	Y	9.4
422b	100% H_2	9.5	N	9.8

Table II. The effect of passivation of carbon acceptors on electrical properties of the base region of InP/InGaAs HBT structures.

Sample	Condition	Hall $p(10^{18}\ \mathrm{cm}^{-3})$	Hall $\mu(\mathrm{cm}^2/\mathrm{Vs})$	TLM $R_s(\Omega/\mathrm{sq.})$	TLM (estimated) $p(10^{18}\ \mathrm{cm}^{-3})$
Base doping calibration	as-grown	3	71	—	—
Base doping calibration	annealed	12	65	—	—
HBT	as-grown	—	—	1350	7
HBT	etched emitter/annealed	—	—	800	12
HBT	annealed/etched emitter	—	—	1620	6
pseudo-HBT	as-grown	6.8	67	—	—
pseudo-HBT	etched emitter/annealed	12	65	—	—
pseudo-HBT	annealed/etched emitter	5.3	65	—	—

emitter ($HCl{:}H_2O$ at room temperature), so the etch is not the source of the passivation.

These results show that acceptor passivation did occur in the base region of these devices, in contrast to the case of the InGaP/GaAs HBTs described earlier. The base region, however, was not as highly passivated as the base doping calibration layer. It also appears that hydrogen may not be able to escape the base during an anneal at 400° C if the emitter is in place. This could be due to trapping of positively ionized hydrogen (H^+) in the base region by the built-in fields at the base-emitter and base-collector *p-n* junctions.

The fact that passivation occurs in the base region implies that either hydrogen is incorporated during growth of the C-doped InGaAs base, or that hydrogen can penetrate the *n*-type InGaAs cap and InP emitter to reach the base during cool-down. To find out whether hydrogen could be incorporated during growth, two more samples identical to the base doping calibration layer were grown, but cooled under different conditions. For the first sample, the flow of AsH_3 was stopped immediately after growth, and the sample was cooled in a 100% H_2 ambient. The as-grown hole concentration was $\sim 5 \times 10^{18}\ \mathrm{cm}^{-3}$, and increased to $\sim 1.2 \times 10^{19}\ \mathrm{cm}^{-3}$ after annealing. For the second sample, the flow of AsH_3 was also stopped immediately after growth, but the substrate temperature was then maintained at 500° C for 5 minutes in a 100% H_2 ambient before cooling in H_2. The as-grown hole concentration in this case was $\sim 9 \times 10^{18}\ \mathrm{cm}^{-3}$. The fact that less acceptor passivation occurred in the second sample suggests that hydrogen was annealed out of the sample during the 5 minute in situ anneal in H_2—a net flow of hydrogen out of the sample occurred during this time. In other words, much of the passivation in the first sample (and in the base of the HBT structure) was due to hydrogen incorporated during growth. We have not attempted to determine the source of the hydrogen incorporated during growth, and cannot rule out the possibility that hydrogen from the column III metalorganic sources could play a role, together with AsH_3 and H_2.

We have also grown 1000Å-thick C-doped InGaAs layers (at ~525° C) with an *n*-type InP cap to investigate the effect of *n*-type cap layers on trapping of hydrogen in C-doped InGaAs. The *n*-InP cap layers were grown at 525° C or 625° C. In the case of growth at 525° C, a 6 second pause was used to switch from AsH_3 to PH_3 between growth of the InGaAs and InP. In the case of growth of the InP cap at 625° C, a 4 minute growth pause under an AsH_3/H_2 ambient was used to raise the temperature from 525° to 625° C following growth of the InGaAs. A similar growth pause was used for the InP/InGaAs HBT structures described earlier. The hole concentration of the C-doped InGaAs layers was then measured using Hall effect after removal of the InP cap by selective etching. The as-grown hole concentration of the InGaAs was $\sim 4\text{–}5 \times 10^{18}\ \mathrm{cm}^{-3}$ when the InP cap was grown at 525° C, and $\sim 6\text{–}7 \times 10^{18}\ \mathrm{cm}^{-3}$ when the InP cap was grown at 625° C. In both cases, the hole concentration after annealing at 400° C in N_2 (with the InP cap already etched off) was $\sim 1.2 \times 10^{19}\ \mathrm{cm}^{-3}$. Thus it appears as though some hydrogen may leave the InGaAs layer during the growth pause and heating to 625° C, resulting in less passivation.

IV. SUMMARY AND CONCLUSIONS

We have shown that the post-growth cool-down is very important in determining the amount of hydrogen passivation in heavily C-doped GaAs grown by MOCVD. The fraction of C acceptors passivated is highest for the most heavily doped samples. This passivation can be reversed by annealing in a hydrogen-free ambient at ~400° C. Nearly 100% electrical activation of C is observed for hole concentrations as high as $3.6 \times 10^{20}\ \mathrm{cm}^{-3}$ after annealing at 400° C in N_2. No measurable passivation was observed, however, in the C-doped base region of InGaP/GaAs HBTs, suggesting that very little hydrogen is incorporated during growth at 625° C, and that H may be unable to incorporate in the buried C-doped GaAs base layer during post-growth cool-down.

Heavily C-doped $In_{0.53}Ga_{0.47}As$ layers are even more susceptible to passivation during post-growth cool-down. All of the cooling ambients studied (AsH_3/H_2, PH_3/H_2, and 100% H_2) resulted in measurable passivation. Hydrogen is also incorporated during growth of C-doped InGaAs at ~525° C, and leads to significant passivation in the base region of InP/

InGaAs HBTs with a C-doped base. Further work is required to determine the optimal scheme for growth and processing of these HBTs to minimize the effects of hydrogen passivation.

We have identified three important parameters which affect the hydrogen passivation of heavily C-doped GaAs and InGaAs grown by MOCVD: (1) the post-growth cool-down ambient; (2) the acceptor concentration; and (3) the location of the C-doped layer in the device structure. The results of this study, together with work by Antell *et al.*[23] and Cole *et al.*[24] on p-type InP, suggest that the effect of the cool-down ambient on acceptor passivation is an important consideration for growth of p-type semiconductors by MOCVD.

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