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# Effect of post-growth cooling ambient on acceptor passivation in carbon-doped GaAs grown by metalorganic chemical vapor deposition

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The degree of unintentional hydrogen passivation of acceptors in heavily C-doped GaAs ( $p > 10^{18} \text{ cm}^{-3}$ ) grown by metalorganic chemical vapor deposition has been found to be a strong function of post-growth cool-down ambient. The carbon concentration in the GaAs and the amount of  $\text{AsH}_3$  in the cool-down ambient are the most important factors affecting passivation. Carbon acceptors can be reactivated by annealing in  $\text{N}_2$ , then repassivated by heating and re-cooling in an  $\text{AsH}_3/\text{H}_2$  or  $\text{PH}_3/\text{H}_2$  ambient. Secondary ion mass spectrometry analysis shows that the hydrogen concentration is significantly higher in a C-doped GaAs surface layer which is exposed to the cool-down ambient than in a layer which is buried beneath  $n$ -type GaAs. This result is consistent with observations in  $n$ - $p$ - $n$  heterojunction bipolar transistor structures, where the fraction of C acceptors passivated in the base region is found to be less than in a single layer grown under identical conditions. Be-doped GaAs grown by gas-source molecular beam epitaxy has also been heated and cooled in  $\text{AsH}_3$ -containing ambients, but no acceptor passivation is detectable by Hall effect measurements.

It is well established that shallow donors and acceptors in GaAs can be passivated by hydrogen.<sup>1-3</sup> Intentional passivation can be performed by several techniques, and can be used as a processing tool for device applications.<sup>4</sup> Unintentional incorporation of hydrogen in III-V materials during crystal growth and processing is also an important area of research.<sup>5,6</sup> Cole *et al.*,<sup>7</sup> and Antell *et al.*,<sup>8</sup> have shown that the electrical activation of Zn acceptors in  $p$ -type InP grown by metalorganic chemical vapor deposition (MOCVD) can be affected by hydrogen from hydride sources present during the post-growth cool-down.

Carbon has become a commonly used  $p$ -type dopant in GaAs due to its low diffusivity, which makes it especially attractive for heterojunction bipolar transistor (HBT) applications. Acceptor passivation due to incorporation of hydrogen during growth has been reported in carbon-doped GaAs and AlGaAs grown by metalorganic molecular beam epitaxy (MOMBE)<sup>9</sup> and MOCVD.<sup>10-14</sup> Woodhouse *et al.* have reported partial passivation of C-doped GaAs upon annealing at 950 °C in an  $\text{AsH}_3/\text{He}$  ambient,<sup>15</sup> and have speculated that hydrogen could be incorporated into MOCVD-grown GaAs from  $\text{AsH}_3$  or  $\text{H}_2$  during post-growth cooling.<sup>16</sup> In this letter we report that the hydrogen passivation of C acceptors in MOCVD-grown GaAs is highly dependent on the ambient present during the cool-down following growth, and that this has important implications for growth of  $n$ - $p$ - $n$  HBTs.

All growths for this study were performed at 76 Torr. Trimethylgallium (TMGa) and arsine ( $\text{AsH}_3$ ) were used as the growth precursors, and disilane ( $\text{Si}_2\text{H}_6$ ) and carbon tetrachloride<sup>17</sup> ( $\text{CCl}_4$ ) were used as dopant sources. A series of C-doped GaAs layers ( $t=4000 \text{ Å}$ ,  $2 \times 10^{18} \text{ cm}^{-3} < p < 3.8 \times 10^{20} \text{ cm}^{-3}$ ) were grown at 575–625 °C on semi-insulating GaAs substrates and characterized by Hall effect. The doping level was varied by changing the  $\text{CCl}_4$  flow rate, growth temperature, and V/III ratio. The standard cool-down sequence following growth consisted of

maintaining the  $\text{H}_2$  and  $\text{AsH}_3$  flows used during growth until the substrate temperature reached 250 °C, at which time the  $\text{AsH}_3$  flow was stopped. Samples were then cooled to room temperature in  $\text{H}_2$ .

The hydrogen passivation was reversed by annealing in a 100%  $\text{N}_2$  ambient in an alloy station at  $\sim 400$  °C for 5 min. The fraction of C acceptors initially passivated was then determined by comparing the carrier concentration measured by Hall effect before and after annealing. In order to study the effect of the cooling ambient on acceptor passivation without the influence of hydrogen incorporated during growth, samples were annealed in  $\text{N}_2$  in the alloy station to reverse the original passivation, then heated to 500 °C, and cooled in  $\text{AsH}_3/\text{H}_2$ ,  $\text{PH}_3/\text{H}_2$ , or  $\text{H}_2$  in the MOCVD reactor. The fraction of acceptors passivated was then determined by comparing the hole concentration to that in a sample which was only annealed in  $\text{N}_2$ .

The hole concentration after annealing at  $\sim 400$  °C in  $\text{N}_2$  ( $p_{\text{annealed}}$ ) is equal, within experimental uncertainty, to the total carbon concentration ( $[\text{C}]$ ) determined by secondary ion mass spectrometry (SIMS),<sup>18</sup> and we assume here that  $p_{\text{annealed}} = [\text{C}]$ . The discrepancy between  $p_{\text{as-grown}}$  and  $[\text{C}]$  which we have reported for C-doped GaAs grown by MOCVD<sup>19</sup> is due mainly to partial hydrogen passivation, and the fraction of C acceptors passivated will be defined here as  $[\text{HC}]/[\text{C}]$ , where  $[\text{HC}]$  represents the concentration of neutralized C acceptors. Table I gives  $[\text{HC}]/[\text{C}]$  for nine samples for the as-grown case and for the case where samples were annealed in  $\text{N}_2$ , then heated and re-cooled in the original post-growth cooling ambient. Nearly identical results for  $[\text{HC}]/[\text{C}]$  are obtained for samples which are re-heated and re-cooled in the original post-growth cooling ambient without first annealing in  $\text{N}_2$ .

The fraction of acceptors passivated,  $[\text{HC}]/[\text{C}]$ , is highest at very high doping levels, but is significant even for  $[\text{C}] \sim 2 \times 10^{18} \text{ cm}^{-3}$ . The most important point in Table I is that the samples are re-passivated to nearly the same

TABLE I. Hole concentration,  $p$ , and fraction of carbon acceptors passivated,  $[\text{HC}]/[\text{C}]$ , for C-doped GaAs after growth and after recooling in the original  $\text{AsH}_3/\text{H}_2$  cooling ambient

Sample ID No.	$[\text{AsH}_3]/[\text{H}_2]$ in cooling ambient ( $\times 10^{-3}$ )	Annealed in $\text{N}_2$	As-grown		Annealed in $\text{N}_2$ , then heated and re-cooled in original ambient	
		$p_{\text{annealed}} \sim [\text{C}]$ ( $10^{19} \text{ cm}^{-3}$ )	$p_{\text{as-grown}}$ ( $10^{19} \text{ cm}^{-3}$ )	$[\text{HC}]/[\text{C}]$	$p$ ( $10^{19} \text{ cm}^{-3}$ )	$[\text{HC}]/[\text{C}]$
447	5.0	0.19	0.16	0.16	0.15	0.21
448	5.0	0.47	0.34	0.28	0.37	0.21
449	5.0	1.57	1.18	0.25	1.13	0.28
450	5.0	3.54	2.08	0.41	2.39	0.32
451	2.5	6.34	3.75	0.41	4.14	0.35
452	1.0	11.9	6.87	0.42	6.65	0.44
455	2.5	15.7	7.76	0.51	8.08	0.49
453	1.0	24.9	13.9	0.44	12.8	0.49
454	0.5	38.1	20.1	0.47	18.8	0.51

level after being heated and re-cooled in the original cool-down ambient. This data suggests that  $[\text{HC}]/[\text{C}]$  is a function of the cooling ambient and the crystal ( $E_f$  or  $[\text{C}]$ ), but independent of growth conditions. This does not preclude the possibility of H incorporation during growth, but does show that  $[\text{H}]$  and  $[\text{HC}]$  may be altered during the cool-down.

Growth of sample 451 was repeated twice, but the  $\text{AsH}_3$  flow was shut off immediately after each growth and post-growth cooling took place in a  $\text{PH}_3/\text{H}_2$  ambient ( $[\text{PH}_3]/[\text{H}_2] = 10^{-2}$ ) or a 100%  $\text{H}_2$  ambient. The fraction of C acceptors passivated was  $[\text{HC}]/[\text{C}] \sim 0.20$  for cooling in  $\text{PH}_3/\text{H}_2$ , and  $\sim 0.04$  for cooling in  $\text{H}_2$ . The influence of different cooling ambients on acceptor passivation was investigated further by annealing the samples listed in Table I in  $\text{N}_2$ , then heating and re-cooling in  $\text{AsH}_3/\text{H}_2$  or  $\text{PH}_3/\text{H}_2$ . These results are shown in Fig. 1. The data clearly show that  $\text{AsH}_3$  is a more efficient source of H than  $\text{PH}_3$ . We have also found that cooling in a 100%  $\text{H}_2$  ambient results in very little passivation ( $[\text{HC}]/[\text{C}] < 0.1$ ). These results are consistent with the fact that the As-H bond in  $\text{AsH}_3$  is weaker than the P-H bond in  $\text{PH}_3$ , and both are less stable than  $\text{H}_2$ . We have also heated and cooled Be-doped GaAs samples grown by gas-source molecular beam epitaxy ( $t = 3500 \text{ \AA}$ ,  $5 \times 10^{18} \text{ cm}^{-3} < p < 6 \times 10^{19} \text{ cm}^{-3}$ ) in these ambients. No decrease in hole concentration was ob-

served for these samples, indicating that the Fermi level is not the only property of the crystal which affects passivation during cool-down. This difference in behavior is likely related to the fact that C is the most efficiently passivated among acceptors in GaAs,<sup>20</sup> and that the dissociation energy of the C-H complex is larger than for Be-H.<sup>21</sup>

Several pieces of sample 454 were heated to  $\sim 500^\circ\text{C}$  in  $\text{H}_2$ , cooled to a temperature  $T_0$  in  $\text{H}_2$ , and cooled from  $T = T_0$  to  $T \sim 250^\circ\text{C}$  in an  $\text{AsH}_3/\text{H}_2$  ambient where  $[\text{AsH}_3]/[\text{H}_2] \sim 10^{-2}$ . We have found that  $[\text{HC}]/[\text{C}]$  is only significant if  $T_0 > 400^\circ\text{C}$ , indicating that the hydrogen is trapped within the crystal during the post-growth cool-down when  $400^\circ\text{C} < T < 500^\circ\text{C}$ . A plausible explanation for the data presented here is that  $[\text{HC}]/[\text{C}]$  is determined by a balance between in-diffusion and out-diffusion of H at the crystal surface which exists during cool down. The in-diffusion rate may be a strong function of the availability of atomic hydrogen, supplied by the decomposition of  $\text{AsH}_3$ , and the concentration of C acceptors (bonding sites) in the GaAs. The out-diffusion rate could depend on  $[\text{H}]$  in the crystal, and on  $[\text{C}]$  as a result of multiple retrapping events which slow the out-diffusion of H, or as a result of the potential barrier formed due to surface Fermi-level pinning which may retard out-diffusion of  $\text{H}^+$ . The H depth profile determined using SIMS is flat, so the H diffusion rate in the crystal is not a rate-limiting factor for these thin layers.

Figure 2 shows the SIMS depth profiles for a  $n$ - $p$ - $n$ - $p$  structure as-grown and after annealing in  $\text{N}_2$ . The C-doped ( $p$ -type) layers were grown under conditions identical to sample 451. All layers of this structure were grown at  $\sim 625^\circ\text{C}$  with  $[\text{AsH}_3]/[\text{H}_2] = 2.5 \times 10^{-3}$ , and post-growth cooling to  $\sim 250^\circ\text{C}$  also took place in this ambient. The profiles were obtained using a  $\text{Cs}^+$  primary beam and negative secondary ion detection. The C, Si, and H concentration data were obtained by comparison with ion-implanted standards (C, Si, and deuterium). The experimental error is believed to be  $\pm 30\%$  for C, and  $\pm 50\%$  for H under these conditions, while the background levels are  $\sim 3 \times 10^{17} \text{ cm}^{-3}$  for C and  $\sim 3 \times 10^{18} \text{ cm}^{-3}$  for H.

The H depth profile for the as-grown case shows that  $[\text{H}]$  is significantly higher in the upper C-doped layer than in the buried C-doped layer. This suggests that hydrogen

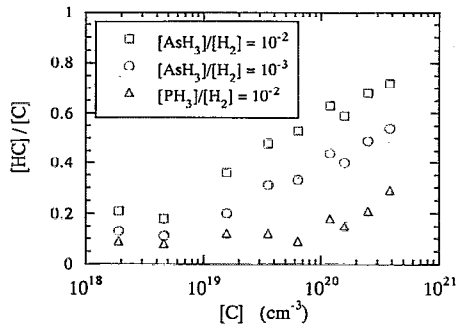


FIG. 1. The fraction of C acceptors passivated by hydrogen,  $[\text{HC}]/[\text{C}]$ , as a function of carbon concentration,  $[\text{C}]$ , for samples heated to  $500^\circ\text{C}$  and cooled in an  $\text{AsH}_3/\text{H}_2$  or  $\text{PH}_3/\text{H}_2$  ambient. All samples were first annealed at  $\sim 400^\circ\text{C}$  in  $\text{N}_2$  to reverse the original passivation.

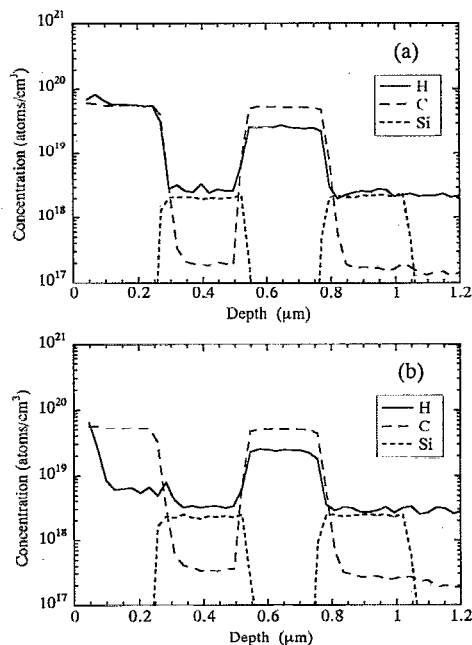


FIG. 2. Atomic concentration of H, C, and Si vs depth in a GaAs *n-p-n* structure (a) as-grown, and (b) annealed at  $\sim 400^\circ\text{C}$  in  $\text{N}_2$  for 5 min. In the as-grown case, (a), [H] is significantly higher in the upper C-doped layer than in the buried C-doped layer. After annealing, (b), [H] in the upper layer is reduced to near the SIMS resolution limit, while [H] is unchanged in the buried layer.

was incorporated during growth at  $\sim 625^\circ\text{C}$ , and that additional hydrogen entered the surface layer during the cool-down. A similar structure was grown at  $\sim 575^\circ\text{C}$ , and for this structure [H] in the buried layer was significantly higher than for growth at  $625^\circ\text{C}$ , suggesting that growth temperature is important in determining the amount of H incorporated during growth. A thin *n*-type surface layer has been reported to block hydrogenation of *p*-type Si and GaAs during exposure to a hydrogen or deuterium plasma.<sup>22,23</sup> Figure 2(a) shows that the *n*-type GaAs layer can similarly “block” in-diffusion of H during the cool-down. We have also found that  $[\text{HC}]/[\text{C}]$  is significantly lower in the C-doped base region of InGaP/GaAs HBTs than in identically grown C-doped GaAs layers where the surface is exposed during cool-down.<sup>18</sup>

Figure 2(b) shows that [H] is clearly reduced in the upper C-doped layer due to out-diffusion of H from the surface during annealing. The hydrogen concentration is unchanged, however, in the buried C-doped layer. Thus, the *n*-type layer can also block out-diffusion of H which is incorporated during growth. The SIMS data is consistent with our observations for InP/InGaAs HBTs, where the *n*-type InP emitter must be removed before annealing in order to reverse passivation in the C-doped InGaAs base.<sup>18</sup> This trapping of H may be related to the built-in fields of the *p-n* junctions which could inhibit out-diffusion of positively ionized hydrogen ( $\text{H}^+$ ).

In conclusion, we have identified a number of important issues related to growth and processing of HBTs grown by MOCVD. Passivation of C acceptors can occur as a result of incorporation of hydrogen during growth or

during the post-growth cool-down. The degree of passivation in a C-doped surface layer is highly dependent on the cooling ambient and the carbon concentration, and originates mainly from  $\text{AsH}_3$ . Cooling of Be-doped GaAs in an  $\text{AsH}_3$ -containing ambient did not result in acceptor passivation, indicating that the acceptor species is an important factor. An *n*-type layer (such as an emitter in a HBT) can inhibit diffusion of H into a buried C-doped GaAs layer during cool-down, and can also block out-diffusion of H incorporated during growth. Further study will be necessary to resolve issues related to the stability of hydrogen passivation during device processing and operation.

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