CHARACTERIZATION OF CARBON INDUCED LATTICE CONTRACTION OF HIGHLY CARBON DOPED InGaAs

Delong Cui, Dimitris Pavlidis, and Andreas Eisenbach
Solid State Electronics Laboratory, Department of Electrical Engineering and Computer Science,
The University of Michigan, Ann Arbor, MI 48109, USA
Phone: +1 (734) 647-1778, Fax: +1 (734) 763-9324, E-mail: pavlidis@umich.edu

Abstract

Lattice contraction introduced by the smaller covalent radius of carbon (77pm) relative to arsenic (120pm), gallium (126pm), and indium (144pm) has been observed in highly carbon doped GaAs [1,2,3]. This paper addresses similar effects in heavily doped InGaAs:C layers, which find applications as the base of InP/InGaAs heterojunction bipolar transistors (HBTs). Heavily carbon doped InGaAs epilayers ($p>1\times10^{19}cm^{-3}$) have been grown by metalorganic chemical vapor deposition (MOCVD) using CBr_4 as the carbon precursor. The lattice contraction effect induced by carbon incorporation has been studied in such samples by extending the technique previously reported for heavily doped GaAs:C. High-resolution double crystal x-ray diffraction (DXRD) as well as Hall measurements have been performed for this purpose. The experiments clarify the way lattice contraction takes place in case of strong carbon incorporation in InGaAs:C samples. They also show that InGaAs:C becomes increasingly compensated as the doping concentration increases. The study has direct impact on the development of high quality InP-based HBTs.

I. Introduction

Carbon is an amphoteric impurity in InGaAs and behaves as acceptor or donor depending on the lattice site occupied. The most commonly used p-dopant in MOCVD grown InGaAs is Zn. However, Zn exhibits significant diffusion [4,5]. On the other hand, carbon doped p-type InGaAs is very attractive for high performance InGaAs/InP HBTs due to its much lower diffusivity compared with traditionally used dopants such as Zn. The amphoteric nature of carbon dopants makes it difficult to obtain p-type carbon doped InGaAs by MOCVD growth. To improve the doping concentration of carbon-doped p-type InGaAs by MOCVD, low growth temperature and low V/III ratio are necessary [6,7,8]. It is therefore important to study the amphoteric nature of carbon doped InGaAs.

The lattice contraction introduced by the smaller covalent radius of carbon (77pm) relative to arsenic (120pm) and gallium (126pm) has been observed in highly carbon doped GaAs and used to characterize the carbon self-compensation by several groups. The atomic and covalent radii of the elements involved are provided in Table 1. Experimental relations between lattice mismatch and the total carbon concentration were obtained and reported [1,2,3]. A similar approach cannot be easily used to analyze C-doped InGaAs because of the ternary nature of this material system. The lattice parameters of the [001] growth plane can be easily determined by double-crystal x-ray diffractometry with [004] Bragg reflection. A relation between the lattice mismatch and the total carbon concentration for heavily C-doped InGaAs was developed in this paper. This relation provides a more complete form of previously reported trends of this type. The equation was used to calculate the total number of carbon atoms incorporated in the material. Combined with Hall measurements, it was used to study the doping mechanisms for heavily carbon doped InGaAs material.

Element	C	In	Ga	As
Atomic Radii (pm)	70	155	130	115
Covalent Radii (pm)	77	144	126	120

Table 1: Atomic and Covalent Radii of Carbon, Indium, Gallium and Arsenic.

II. Material Growth and Characterization

Carbon doped InGaAs samples were grown using our in-house EMCORE GS3200 LP-MOCVD system. The system has a vertical reactor with rotating susceptor to improve the uniformity of the material. TMIn and TMGa were used as In and Ga sources, respectively. Pure 100% arsine and phosphine were used as group V precursors. Liquid CBr_4 was used as carbon precursor. The pressure of the growth chamber was maintained at 60torr and the susceptor was rotated at 100rpm to provide the best sample uniformity. All growth experiments were carried out on Fe-doped semi-insulating InP substrates. In order to achieve heavily carbon-doped p-type InGaAs by MOCVD, low growth temperature and low V/III ratio are required. Temperatures of 450°C and 430°C were

used for the growth of heavily p-doped C-InGaAs layers in order to obtain the best trade-off between doping concentration and surface morphology. Hydrogen passivation of the carbon acceptors takes place during growth and de-passivation was therefore necessary to free C-H bonds. This was achieved by post-growth annealing at 550°C in N_2 ambient for 30 seconds using rapid thermal annealing (RTA). Doping concentration and mobility of the samples were measured by using Hall measurements. Fig. 1 shows the effect of growth temperature on p-type doping concentration of carbon doped InGaAs. The flow rate of CBr_4 was kept constant for the samples under study. The figure also shows that the doping concentration increases after RTA annealing by freeing passivated carbon atoms. P-type doping concentration increases almost 50% after the post-growth annealing depending on the in-situ doping concentration

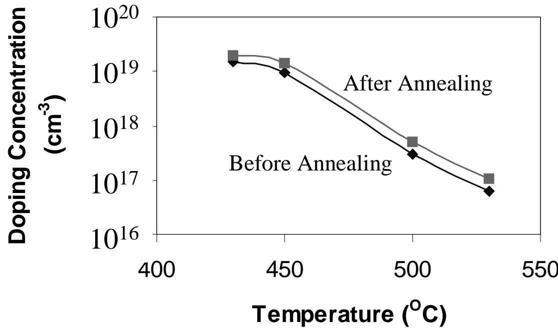

Fig. 1. Doping concentrations in InGaAs:C as a function of growth temperature using CBr_4 as precursor.

III. Carbon Induced Lattice Contraction

A series of heavily carbon-doped p-type InGaAs samples with a thickness of 0.50 μm was grown by MOCVD in this study. The lattice parameters of the [001] growth plane of heavily carbon-doped p-type InGaAs:C samples can be determined by double-crystal x-ray diffractometry with [004] Bragg reflection. All the double crystal x-ray data reported in this study were obtained from a Rigaku double crystal diffractometer (DXRD) with a conventional 1.5kW generator fitted with a Cu target ($\lambda_{Cu}K_{\alpha 1}$=0.1540562nm). The carbon induced lattice contraction normal to the growth plane $\Delta a_{\perp}/a$ can be calculated from the measured angular peak separation between InGaAs:C samples and InP substrates and is expressed as follows

$$\frac{\Delta a_{\perp}}{a} = -\Delta\theta \times \cot(\theta_B) \qquad (1)$$

where Δθ is the angular separation between the epilayer peak and substrate peak, and θ_B is the Bragg angle of the (004) InP substrate reflection.

The strain-free lattice mismatch Δa/a can be derived from $\Delta a_{\perp}/a$ as following:

$$\frac{\Delta a}{a} = \frac{c_{11}}{c_{11}+2c_{12}}\frac{\Delta a_{\perp}}{a} = 0.503\frac{\Delta a_{\perp}}{a} \qquad (2)$$

where Δa/a is the strain free lattice mismatch determined from the measured lattice mismatch of the tetragonally distorted epilayer normal to the growth plane $\Delta a_{\perp}/a$ and the elastic constants c_{11} and c_{12} of InGaAs.

The results obtained from the above calculations are shown in Fig. 2. Carbon induced lattice contraction effects become increasingly important as the carbon doping concentration increases in the heavily carbon doped p-type InGaAs samples of this work. The doping concentration was evaluated from Hall measurements for all the samples under this study. The carbon induced lattice contraction increases from 1.3×10^{-4} at relatively lower doping concentrations ($5\times10^{18}cm^{-3}$) to more than 1×10^{-3} at higher doping concentrations. A maximum lattice contraction of 2×10^{-3} was observed for a doping concentration of $5\times10^{19}cm^{-3}$.

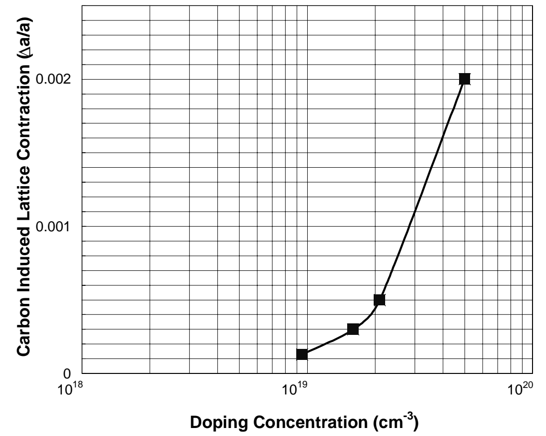

Fig. 2. Carbon induced lattice contraction Δa/a in InGaAs:C determined from DXRD measurements as a function of doping concentration.

The above results are in agreement with expected characteristics since an increased number of carbon atoms is incorporated into the heavily carbon doped InGaAs samples as the doping concentration increases. As a result, carbon atom induced lattice contraction becomes more severe and the lattice mismatch increases.

IV. Discussion

Fig. 2 also shows that the carbon induced lattice contraction is not proportional to the doping concentration. Instead, it becomes increasingly larger as the doping concentration increases. The above phenomena indicate that more and more carbon atoms need to be incorporated in order to reach higher doping

concentrations. In other words, the material becomes more compensated as the doping concentration increases.

The relation between carbon induced lattice contraction and total carbon atoms incorporated in heavily doped GaAs:C can be expressed as [1,3]

$$\Delta a = \frac{4}{\sqrt{3}} \frac{\Delta r_{Ga} N_{C,Ga} + \Delta r_{As} N_{C,As}}{2.2\times10^{22}} \quad (3)$$

where Δa represents the change in strain-free epilayer lattice constant, which can be determined from the DXRD measurements as addressed above. Δr_{Ga}, Δr_{As} are the covalent radius differences between C and Ga or As, respectively. $N_{C,Ga}$, $N_{C,As}$ represent carbon atoms occupying Ga or As site, respectively.

The approach reported for analyzing GaAs:C [1,3] was extended to InGaAs:C by using Vegard's Law and considering the covalent radii of the elements involved that are summarized in Table 1. As can be seen from the data of Table 1, the covalent radii of In, Ga, and As are very similar while the covalent radius of carbon is significantly smaller. The resulting lattice contraction expression in the case of InGaAs:C is as following

$$\Delta a = \frac{4}{\sqrt{3}} \left[\frac{\left(\Delta r_{Ga} N_{C,Ga} + \Delta r_{As} N_{C,As}\right)(1-x)}{2.2\times10^{22}} + \frac{\left(\Delta r_{In} N_{C,In} + \Delta r_{As} N_{C,As}\right)x}{1.8\times10^{22}} \right] \quad [4]$$

where x is the In composition and is expected to be 0.53 for lattice matched $In_xGa_{1-x}As$. Δr_{Ga}, Δr_{As}, Δr_{In} are the covalent radius differences between C and Ga, As, and In, respectively. From Table 1, Δr_{Ga}, Δr_{As}, Δr_{In} can be found to be 0.49Å, 0.43Å and 0.67Å, respectively. $N_{C,Ga}$, $N_{C,In}$, $N_{C,As}$ represent carbon atoms occupying Ga, In, and As sites, respectively.

If the total number of carbon atoms is considered to be the sum of atoms incorporated into the In, Ga and As sites, in other words, if one assumes that post-growth annealing frees all the carbon hydrogen complexes, the total carbon concentration can be expressed as:

$$N_{total} = N_{C,As} + N_{C,Ga} + N_{C,In} \quad (5)$$

The assumption of no carbon hydrogen complexes after post-growth annealing is reasonable as can be observed from Fig. 1, which shows an increased doping concentration with annealing. It was also pointed out from a previous study by the authors regarding the FTIR spectrum for the heavily carbon doped InGaAs samples before and after post-growth annealing that a significant part of this improvement results from the depassivation of carbon hydrogen complexes upon post-growth annealing [9]. Thus, the remaining carbon hydrogen complexes should be negligible after post-growth annealing is performed. This was also verified by SIMS spectra for the same samples.

The doping concentration determined by Hall measurements can be expressed as the difference between the carbon atoms occupying group V site and those occupying group III site.

$$P_{Hall} = N_{C,As} - N_{C,Ga} - N_{C,In} \quad (6)$$

where P_{Hall} is the doping concentration measured from Hall measurements.

Since there are three variables ($N_{C,Ga}$, $N_{C,In}$, $N_{C,As}$) and only two equations (Eqs. 2 and 3), an additional equation was added by postulating the ratio between the carbon atoms occupying the Ga site ($N_{C,Ga}$) and those occupying the In site ($N_{C,In}$). As reported earlier [10,11,12], carbon is expected to occupy the In rather than Ga site due to the weaker bond strength of C-In than C-Ga. Fig. 3 shows the dependence of total carbon atomic concentration on Hall doping concentration for the case where there is no carbon occupying the Ga site and when the ratio between $N_{C,In}$ and $N_{C,Ga}$ is one. The results show that this difference does not translate into a large difference in total carbon concentration. This is easily understood since the In covalent radius is relatively close to that of Ga and, hence, does not result in a significant difference in terms of carbon lattice contraction and total carbon concentration.

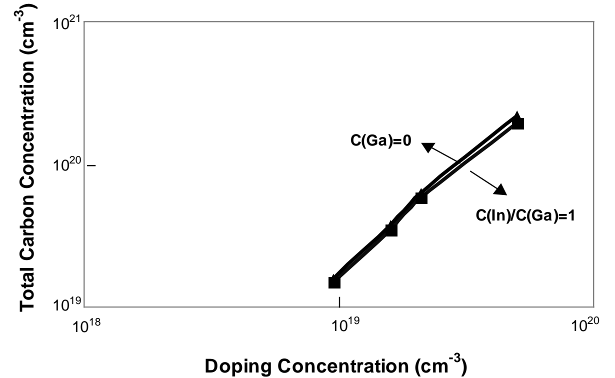

Fig. 3. Total carbon atom concentration of C-InGaAs for samples with different hole concentrations.

Fig. 4 shows the ratio between carbon atoms occupying group III sites and the total carbon concentration. It is shown that as the doping concentration increases in InGaAs:C, more and more carbon atoms are incorporated into group III sites, approaching the concentration of carbon atoms in group V sites. This leads towards a point where acceptor (N_A) and donor (N_D) concentrations might become equal and, thus, the resulting material is compensated. It explains also the fact that post-growth annealing becomes less and less effective as the doping concentration increases.

Since more and more carbon atoms start to occupy group III sites, and the material becomes more compensated as the doping concentration increases, a smaller increase of doping concentration is expected after post-growth annealing. This trend is verified experimentally by comparing the doping concentration improvements after post-growth annealing for InGaAs:C samples with different doping concentrations. A nearly 50% increase was observed for samples with an in-situ doping concentration of $1\times10^{19}cm^{-3}$ while it was less than 30% for samples with an in-situ doping concentration of $2.5\times10^{19}cm^{-3}$.

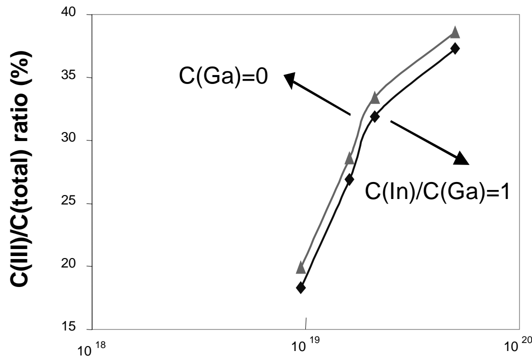

Fig. 4. The ratio of carbon atoms occupying group III (In, Ga) sites to total carbon concentration.

Based on the above discussions, it is concluded that the increase of carbon doping concentration becomes more and more difficult as the doping concentration increases. Although post-growth annealing can improve the in-situ doping concentration significantly by freeing carbon atoms from carbon hydrogen complexes, this increase is expected to be less and less important as the heavily carbon doped p-type InGaAs material becomes more and more compensated. This imposes another challenge in terms of carbon doping InGaAs material by MOCVD, namely how to decrease the self-compensation of heavily p-type doped InGaAs material by carbon atoms which are of amphoteric nature.

It was postulated by our previous study that post-growth annealing not only frees carbon atoms by decomposing the carbon hydrogen complexes but also transfers some carbon atoms from group III site to group V site [13]. However, the experiments presented here show that the heavily carbon doped material becomes more and more compensated as the doping concentration increases even after post-growth annealing. Therefore, phenomena of this type should also be suppressed as the doping concentration increases.

V. Conclusion

Overall, lattice contraction effects induced by carbon incorporation have been reported. It has been found that the results of the compensation are relatively independent of whether the carbon occupies the In or Ga site. It has also been shown that C-doped InGaAs becomes more and more compensated as the doping concentration increases. This also explains to certain extent why there is less improvement in doping concentration when post-growth annealing is performed in heavily doped C-InGaAs.

Acknowledgements

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References

[1]. T. J. de Lyon, J. M. Woodall, M. S. Goorsky, and P. D. Kirchner, "Lattice contraction due to carbon doping of GaAs grown by metalorganic molecular beam epitaxy," Appl. Phys. Lett., Vol. 56, pp. 1040-1042, 1990.

[2]. C. Giannini, A. Fischer, C. Lange, K. Ploog and L.Tapfer, "Heavy carbon doping of GaAs grown by solid-source molecular-beam epitaxy," Appl. Phys. Lett., Vol. 61, pp. 183-185, 1992.

[3]. Q. Liu, A. Brennemann, H. Hardtdegen, A. Linder, W. Prost and F.-J. Tegude, "Characterization of hydrogen passivation and carbon self-compensation of highly C-doped GaAs by means of x-ray diffraction," J. Appl. Phys., Vol. 79, pp. 710-716, 1996.

[4]. P. Enquist, J. A. Hutchby, and T. J. D. Lyon, " Growth and diffusion of abrupt zinc profiles in gallium arseide and heterojunction bipolar transistor structures grown by organometallic vapor phase epitaxy," Journal of Applied Physics, vol. 63, pp 4485-4493, 1988.

[5]. K. Hurishma, T. Kobayashi, and U. Gosele, " Abnormal redistribution of Zn in InP/ InGaAs heterojunction bipolar transistor structures," Applied Physics Letters, vol. 60, pp. 2496-3498, 1992.

[6]. C. R. Abernathy, S. J. Pearton, F. Ren, W. S. Hobson, T. R. Fullowan, " Carbon doping of III-V compounds grown by MOMBE," J. of Crys. Growth, Vol. 105, pp. 375-382, 1990.

[7]. T. P. Chin, P. D. Kirchner, J. M. Woodal, and C. W. Tu, " Heavily carbon-doped p- type InGaAs and InGaP by carbon tetracholoride in gas-source molecular beam epitaxy," Appl. Phys. lett., Vol 59, pp. 2865-2867, 1991.

[8]. K. Zhang, W. Hwang, D. L. Miller, and L. W. kapitan, " Carbon doping of InGaAs in solid source molecular beam epitaxy using carbon tetrabromide," Appl. Phys. Lett., Vol. 63, pp. 2399-2401, 1994.

[9]. A. Sibai, F. Ducroquet, K. Hong, D. Cui, D. Pavlidis, M. Melloch, M.A. Reed, "Fourier transform infrared spectroscopy (FTIR), SIMS and Raman scattering of heavily carbon doped MOCVD grown InGaAs," Proceedings of the IEEE Twenty-Fourth International Symposium on Compound Semiconductors, pp. 311-14, 1998.

[10]. H.Ito and T. Ishibashi, "Carbon incorporation in (AlGa)As, (AlIn)As and (GaIn)As ternary alloys grown by molecular beam epitaxy," Jpn. J. Appl. Phys., Vol. 30, pp. 944-947, 1991.

[11]. Hartley, F. and Patai. S., The Chemistry of the Metal-Carbon Bond, Wiley, New York, pp. 53-71, 1982.

[12]. E. Tokumitsu, J. Shirakashi, M. Qi, T. Yamada, S. Nozaki and M. Konagai, "Heavily carbon-doped p-type InGaAs by MOMBE," J. Crys. Growth, Vol. 120, pp. 301-305, 1992.

[13]. K. Hong and D. Pavlidis, "Growth and characterization of heavily carbon doped InGaAs lattice matched to InP by LP-MOCVD using liquid CCl4," J. Electron. Mater. Vol. 25, pp. 449-455.