Lattice contraction due to carbon doping of GaAs grown by metalorganic molecular beam epitaxy

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Epitaxial layers of GaAs have been grown by metalorganic molecular beam epitaxy (MOMBE) with atomic carbon concentrations ranging from 4×10^{17} to 3.5×10^{20} cm^{-3}. The dependences of GaAs lattice parameter and hole concentration on atomic carbon concentration have been determined from x-ray diffraction, Hall effect, and secondary-ion mass spectrometry measurements. For atomic carbon concentrations in excess of 1×10^{19} cm^{-3}, the hole concentrations are less than the corresponding atomic carbon concentrations. Lattice parameter shifts as large as 0.2% are observed for carbon concentrations in excess of 1×10^{20} cm^{-3}, which results in misfit dislocation generation in some cases due to the lattice mismatch between the C-doped epilayer and undoped substrate. Over the entire range of carbon concentrations investigated, Vegard's law accurately predicts the observed lattice contraction.

The incorporation of carbon at concentrations in excess of 1×10^{20} cm^{-3} in films of GaAs and $Al_xGa_{1-x}As$ grown by metalorganic molecular beam epitaxy (MOMBE) has recently emerged as a subject of considerable research interest.[1-7] Because of its much lower diffusion coefficient,[8,9] carbon has been identified as a useful alternative to other *p*-type dopants such as beryllium that are more commonly employed in solid source MBE. Applications such as the heavily doped base layer of the *Npn* heterojunction bipolar transistor that are sensitive to the relative locations of p^+-n junctions and compositional heterojunctions are expected to benefit from the improved control of high concentration *p*-type doping profiles afforded by intrinsic carbon doping from the group III metalorganic sources employed in MOMBE.

It has been observed that films of GaAs grown by MOMBE with trimethylgallium (TMG) as the group III source and either arsine[1-4] or solid arsenic[5-7] as the group V source exhibit hole concentrations in the 10^{19}–10^{21} cm^{-3} range depending on the substrate temperature and V/III ratio employed during growth. For carbon concentrations on the As sublattice in excess of 2.2×10^{20} cm^{-3}, over 1% of the As sites are occupied by carbon atoms. At such a high level of substitutional carbon concentration, the lattice parameter of the doped film might be expected to differ markedly from that of an undoped GaAs layer due to lattice relaxation associated with the smaller covalent radius of carbon (0.77 Å) compared to arsenic (1.20 Å). Results published to date on the lattice parameter of heavily C-doped GaAs films are contradictory, with Putz *et al.*[3] inferring lattice mismatch between C-doped epilayers and GaAs substrates from cross-hatched surface morphology and multiple peaks in x-ray diffraction data, while Saito *et al.*[6,7] claim lattice matching of GaAs films doped with C to a hole concentration of 3.3×10^{20} cm^{-3} with a GaAs substrate. Since residual layer strains and misfit dislocation formation in such C-doped films represent potentially serious consequences of such high doping levels, it is the purpose of this letter to present the results of a study of the variation of lattice parameter with carbon content in films of GaAs grown by MOMBE.

For the purposes of this letter, four samples will be considered. All four layers were grown on (001) GaAs substrates in a Varian Gen II Modular Gas Source MBE system using either TMG or triethylgallium (TEG) as group III precursors. The metalorganic precursors are introduced through a low-pressure injector maintained at 80 °C and are transported by palladium-purified hydrogen carrier gas metered with mass flow controllers. A conventional effusion cell provides an As_4 flux. The relevant growth parameters are summarized in Table I. Three of the samples were grown with the TMG source, which resulted in hole concentrations ranging from 2.5×10^{19} to 1.5×10^{20} cm^{-3}, while the fourth layer was grown with a TEG source that yielded a hole concentration of 4×10^{17} cm^{-3}. In all four samples, an As_4 solid source beam equivalent pressure of 2×10^{-5} Torr was supplied as the group V source. The substrate temperatures were measured with an infrared pyrometer. Carrier concentrations were determined with van der Pauw Hall effect measurements and atomic carbon concentrations were measured with secondary-ion mass spectrometry (SIMS) calibrated with carbon ion-implanted standards.[8,10,11] The lattice parameters of the C-doped films in the [001] growth direction were measured with a double-crystal x-ray diffractometer using the (004) Bragg reflection and Cu $K\alpha$ radiation.

The relationship between hole and atomic carbon concentrations is displayed in Fig. 1. As the SIMS carbon concentration extends beyond 1×10^{19} cm^{-3}, the doping efficiency of the carbon drops below unity. At the highest carbon concentration of 3.5×10^{20} cm^{-3}, the hole concen-

TABLE I. MOMBE growth parameters for carbon-doped GaAs films.

Sample	Growth temperature (°C)	Layer thickness (μm)	Group III source	SIMS carbon ($\times10^{19}$ cm^{-3})
A	600	0.73	TMG	4.0
B	600	7.70	TMG	17
C	500	2.52	TMG	35
D	600	1.70	TEG	0.04

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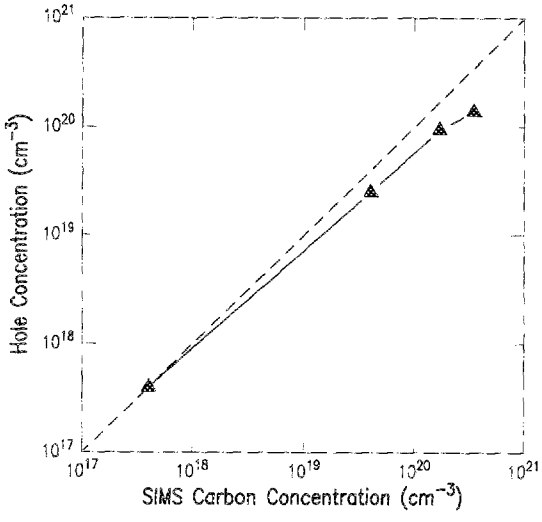

FIG. 1. Relation of hole concentration determined with Hall effect measurements to the total atomic carbon concentration measured with secondary-ion mass spectrometry (SIMS) for carbon-doped GaAs epilayers. The dashed line corresponds to the case of no dopant compensation and unity doping efficiency of the carbon atoms.

trations is only about 40% of the total carbon concentration. This result suggests that a substantial fraction of the carbon impurities are either electrically inactive or are compensated by a donor species. Although carbon has not been observed to be a substitutional donor at low concentrations in epitaxial material grown either by organometallic vapor phase epitaxy or MBE,[12] carbon could perhaps behave as an interstitial donor in a manner similar to zinc[13] or could form complexes with donor-like GaAs point defects.

The x-ray diffraction curves for the four samples are summarized in Fig. 2. At the lowest doping level of 4×10^{17} cm^{-3}, only a single peak corresponding to the (001) GaAs substrate is observed. In the other three heavily C-doped layers, a second peak attributable to the epilayer is observed to shift away from the substrate peak with increasing levels of C doping. The change in epilayer perpendicular lattice parameter, $\Delta a_\perp$, can be determined from the angular peak separation, $\Delta\theta$, with the following relation:

$$\Delta a_\perp / a_{\mathrm{GaAs}} = -\Delta\theta \cot(\theta_B), \tag{1}$$

where a_{GaAs} is the (unstrained) lattice parameter of GaAs and θ_B is the Bragg angle of the (004) substrate reflection. Figure 3 is a plot of the values of $\Delta a_\perp$ determined in this manner as a function of the SIMS atomic carbon concentration. For comparison, the data of Yamada *et al.*[5] on C-doped GaAs layers also grown by MOMBE are displayed. Their data indicate essentially no shift in the GaAs lattice parameter for hole concentrations up to 3×10^{20} cm^{-3}, a result quite different from that which we have observed. The Be-doping data of Lievin *et al.*[14] for solid-source MBE epitaxial material are also included in Fig. 3 since the covalent radius of Be, 0.9 Å, like that of C, is substantially smaller than that of Ga or As. As in the case of the C-doped layers we report here, the substitutional Be doping also resulted in a significant lattice contraction.

The results of Fig. 3 for lattice contraction due to C doping are in good agreement with a simple Vegard's law calculation that assumes a linear variation of the lattice constant with substitutional carbon concentration. This relation can be expressed as

$$\Delta a_\perp = \frac{4}{\sqrt{3}} \frac{(\Delta r_{\mathrm{Ga}} C_{\mathrm{Ga}} + \Delta r_{\mathrm{As}} C_{\mathrm{As}})}{2.22\times10^{22}}, \tag{2}$$

where $\Delta r_{\mathrm{Ga}} = -0.49$ Å is the difference between the C and Ga covalent radii, $\Delta r_{\mathrm{As}} = -0.43$ Å is the corresponding difference between C and As, C_{Ga} is the atomic concentration of C on Ga sites, and C_{As} is the concentration of C on As sites. The theoretical curves in Fig. 3 have been calculated assuming that all the carbon atoms occupy substitutional sites and that $C_{\mathrm{Ga}} = 0.33 C_{\mathrm{As}}$. It should be noted that because the covalent radii of Ga (1.26 Å) and As (1.20 Å)

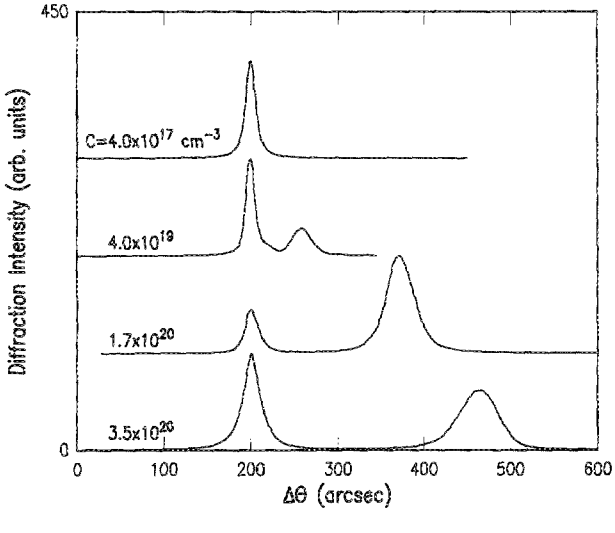

FIG. 2. Double-crystal x-ray diffraction rocking curves for carbon-doped GaAs epilayers.

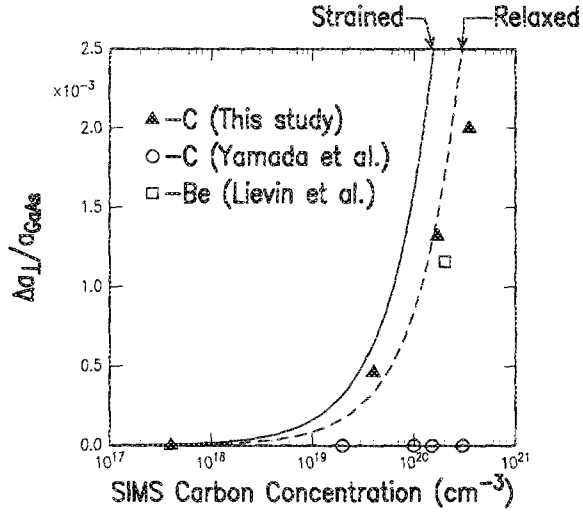

FIG. 3. Plot of relative lattice parameter contraction in the [001] growth direction determined from x-ray diffraction data as a function of atomic carbon concentration measured with secondary-ion mass spectroscopy (SIMS) for carbon-doped GaAs epilayers. The solid and dashed lines represent the predicted contraction based on Vegard's law for coherently strained and completely relaxed epilayers, respectively. The data of Yamada *et al.* (see Ref. 7) for C and of Lievin *et al.* (see Ref. 14) for Be, based on Hall effect measurements, are included for comparison.

differ by less than 5%, the calculation is relatively insensitive to the exact distribution of C between Ga and As sites. The more important assumption implicit in the calculation is that the entire atomic C concentration is substitutional.

Because the perpendicular lattice parameter determined from the x-ray measurement depends on whether the epilayer is pseudomorphically strained to be coherent with the GaAs substrate or is relaxed as a result of misfit dislocation formation, two theoretical Vegard's law lines have been plotted in Fig. 3. The relaxed curve corresponds to Eq. (2) above, while the strained curve accounts for the additional perpendicular lattice parameter mismatch due to the tetragonal distortion along the [001] direction[15,16]:

$$\Delta a_{\perp}\,(\text{strained}) = \frac{(1+\nu)}{(1-\nu)}\,\Delta a_{\perp}\,(\text{relaxed}) = 1.90\Delta a_{\perp}\,(\text{relaxed}), \qquad (3)$$

where a value of $\nu = 0.31$ has been assumed as the Poisson ratio of the GaAs epilayer. The data points for our C-doped layers appear to lie closer to the relaxed curve, which is reasonable given their thickness of several microns. In fact, crosshatching was visible on the surface of sample C under Nomarski microscope, which is indicative of the introduction of misfit dislocations that relieve the elastic strain.

It is clear from the data of Fig. 3 that the experimentally observed lattice contraction for C-doped GaAs films agrees fairly well with the prediction of the Vegard's law analysis for the relaxed case, given the 10–20% relative accuracy of the SIMS carbon concentration determination. This observation appears to rule out any appreciable formation of a precipitated phase of carbon, since the lattice parameter is usually observed to stop changing when dopant precipitation occurs in n-type GaAs.[17,18] The agreement of the Vegard's law calculation and the data of Fig. 3 at doping levels of 10^{20} cm^{-3} suggests that, unlike the case of certain n-type dopants such as tin and tellurium, complicated point defect configurations are not likely to play a role in determining the lattice parameter of heavily carbon-doped GaAs. Compensation of the C_{As} acceptor by C_{Ga} donors, by interstitial carbon donors, or by donor-like GaAs point defects (whose presence presumably did not significantly perturb the substitutional carbon-induced lattice contraction) are three possible explanations for the decrease in p-type doping efficiency that we have observed at high C doping levels. Clearly, further analysis will be required to more completely understand the behavior of C in the GaAs crystal lattice at these extremely high doping levels.

In conclusion, the first data detailing the lattice contraction of MOMBE-grown GaAs due to extremely high C doping levels have been presented. For C concentrations between 1×10^{17} and 3.5×10^{20} cm^{-3}, a Vegard's law analysis of the dependence of lattice parameter on atomic C concentration suggests simple substitutionality of the C dopant. In addition, compensation of the C_{As} acceptor is observed for C concentrations in excess of 1×10^{19} cm^{-3}. Since the GaAs lattice parameter continues to decrease at these high C concentrations, precipitation of the C dopant atoms is considered to be an unlikely source of the compensation.

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[1] N. Putz, E. Veuhoff, H. Heinecke, M. Heyen, H. Luth, and P. Balk, J. Vac. Sci. Technol. B 3, 671 (1985).
[2] M. Weyers, N. Putz, H. Heinecke, M. Heyen, H. Luth, and P. Balk, J. Electron. Mater. **15**, 57 (1986).
[3] N. Putz, H. Heinecke, M. Heyen, P. Balk, W. Weyers, and H. Luth, J. Cryst. Growth **74**, 292 (1986).
[4] H. Heinecke, K. Werner, M. Weyers, H. Luth, and P. Balk, J. Cryst. Growth **81**, 270 (1987).
[5] E. Tokumitsu, Y. Kudou, M. Konagai, and K. Takahashi, J. Appl. Phys. **55**, 3163 (1984).
[6] K. Saito, E. Tokumitsu, T. Akatsuka, M. Miyauchi, T. Yamada, M. Konagai, and K. Takahashi, J. Appl. Phys. **64**, 3975 (1988).
[7] T. Yamada, E. Tokumitsu, K. Saito, T. Akatsuka, M. Miyauchi, M. Konagai, and K. Takahashi, J. Cryst. Growth **95**, 145 (1989).
[8] T. F. Kuech, M.A. Tischler, P.-J. Wang, G. Scilla, R. Potemski, and F. Cardone, Appl. Phys. Lett. **53**, 1317 (1988).
[9] 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).
[10] G. J. Scilla, T. F. Kuech, and F. Cardone, Appl. Phys. Lett. **52**, 1704 (1988).
[11] T. F. Kuech, G. J. Scilla, and F. Cardone, J. Cryst. Growth **93**, 550 (1988).
[12] T. S. Low, B. J. Skromme, and G. E. Stillman, in *Inst. Phys. Conf. Ser. No. 65* (Institute of Physics, Bristol, England, 1983), p. 515.
[13] R. L. Longini, Solid-State Electron. **5**, 127 (1962).
[14] J. L. Lievin, C. Dubon-Chevallier, G. Leroux, J. Dangla, F. Alexandre, and D. Ankri, in *Inst. Phys. Conf. Ser. No. 79* (Institute of Physics, Bristol, England, 1985), p. 595.
[15] W. J. Bartels and W. Nijman, J. Cryst. Growth **44**, 518 (1978).
[16] S. N. G. Chu, A. T. Macrander, K. E. Strege, and W. D. Johnston, Jr., J. Appl. Phys. **57**, 249 (1985).
[17] C. M. H. Driscoll, A. F. W. Willoughby, J. B. Mullin, and B. W. Straughan, *Inst. Phys. Conf. Ser. No. 24* (Institute of Physics, London, England, 1974), p. 275.
[18] J. B. Mullin, B. W. Strautghan, C. M. H. Driscoll, and A. F. W. Willoughby, J. Appl. Phys. **47**, 2584 (1976).