Heavy carbon doping of metalorganic chemical vapor deposition grown GaAs using carbon tetrachloride

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A mixture of 500 ppm CCl_4 in H_2 has been used to grow heavily doped *p*-type GaAs by low-pressure metalorganic chemical vapor deposition with TMGa and AsH_3 as the group III and V sources, respectively. Carbon acceptor concentrations between 1×10^{16} and 1×10^{19} cm^{-3} were obtained. In addition, abrupt carbon-doping profiles were achieved with no noticeable memory effects. Carrier concentration was studied as a function of CCl_4 flow, V/III ratio, growth temperature, and growth rate using electrochemical capacitance-voltage profiling. Carbon incorporation was found to depend on CCl_4 flow, V/III ratio, and growth temperature. Carbon incorporation had no dependence on the growth rate.

Heavily doped *p*-type layers in GaAs are commonly used in several device structures. They are important in diode lasers and in the base region of heterojunction bipolar transistors (HBTs).[1] Magnesium and Zn are commonly used *p*-type dopants in metalorganic chemical vapor deposition (MOCVD), but these dopants exhibit problems in obtaining abrupt doping profiles due to the adsorption of these reactants on the internal surfaces of the growth chamber and gas lines.[2–4] In addition, rapid diffusion of group IIA and IIB elements in GaAs can also lead to dopant redistribution during growth and subsequent processing.

Carbon has been proposed as an alternative dopant to Mg and Zn.[5–7] Carbon is expected to incorporate only as a shallow acceptor on an As site with very little interstitial incorporation, even at high doping levels.[8] As a result, carbon is expected to have greatly improved diffusion characteristics in comparison to Mg and Zn.[8–11]

Several methods for carbon doping have been proposed. Intentional addition of carbon using a number of hydrocarbon sources has either not been successful, or has led to films of low carbon content.[9,12] One researcher has successfully added carbon to GaAs layers with trimethylarsenic.[8] In this work we show that CCl_4 may be used to controllably obtain *p*-type GaAs with carrier concentrations between 1×10^{16} and 1×10^{19} cm^{-3} in low-pressure MOCVD-grown layers. In addition, we demonstrate that CCl_4 doping yields excellent doping abruptness and does not display the memory effects inherent with Mg and Zn doping. These layers are suitable for high doping applications such as HBTs and diode lasers.

The MOCVD reactor used in this work is an Emcore GS3100. The reactor chamber is constructed of stainless steel, with copper gaskets and Viton O-rings used for all seals. The CCl_4 source, provided by Matheson, was a 500 ppm mixture of CCl_4 in H_2. Trimethylgallium (Alfa), and 100% AsH_3 (Phoenix Research) were the group III and V sources, respectively. All growths were carried out on 2° off (100) oriented GaAs substrates with a substrate rotation speed of 1500 rpm. The reactor pressure was 100 Torr with a total H_2 flow of 9 ℓ/min. The growth temperature was varied from 620 to 760 °C, and the growth rate ranged from 700 to 1300 Å/min. The V/III ratio was varied from 32 to 129 in this study. Undoped GaAs samples grown at 700 °C, with a growth rate of 1300 Å/min, an AsH_3 flow of 100 sccm, and a V/III ratio of 64 had *n*-type background carrier concentrations of 1×10^{15} cm^{-3}.

To study the growth temperature, growth rate, and V/III dependence of carbon incorporation, the sequence of layers shown in Table I was grown during a single growth run at a constant temperature. The CCl_4 flow was held constant while the growth rate and V/III ratio were varied independently. Each layer in the sequence had a thickness of about 1 μm, which was sufficient for carrier concentration measurement with a Polaron PN4100 electrochemical profiler. The layer sequence was repeated for growth temperatures between 640 and 760 °C.

The carrier concentration as a function of V/III ratio at three different growth temperatures is shown in Fig. 1 for a CCl_4 flow of 100 sccm. The *p*-type carrier concentration is highest at low V/III ratios, and appears to level out at high V/III ratios for each temperature. A similar trend is typically observed in undoped MOCVD-grown GaAs, so it is not clear to what extent carbon incorporation from the CCl_4 is a function of the V/III ratio. The carrier concentration is less dependent upon the V/III ratio at lower growth temperatures. Figure 1 demonstrates the strong growth temperature dependence of carbon incorporation. By varying the growth temperature between 620 and 760 °C, carrier concentrations ranging from 1×10^{19} to 1×10^{16} cm^{-3} were obtained.

TABLE I. Layer sequence grown at a constant temperature to measure the effects of V/III ratio and growth rate on carbon incorporation with a constant CCl_4 flow rate of 100 sccm. This structure was repeated for temperatures between 640 and 760 °C.

Layer	1	2	3	4
AsH_3 flow (sccm)	50	50	100	100
TMGa flow (sccm)	30	15	30	15
Growth rate (Å/min)	1333	667	1333	667
V/III ratio	32	64	64	128

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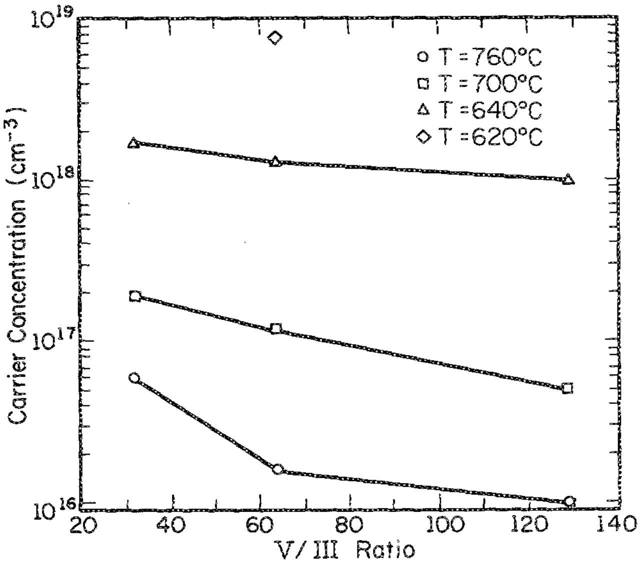

FIG. 1. Variation of carrier concentration with V/III ratio with a fixed CCl_4 flow of 100 sccm for growth temperatures between 640 and 760 °C. Carrier concentration is a strong function of growth temperature, and is least dependent upon V/III ratio at lower growth temperatures. A single layer, grown at 640 °C and a V/III ratio of 64, had a carrier concentration of 8×10^{18} cm^{-3}.

The growth rate dependence of carrier concentration was studied for growth temperatures between 640 and 760 °C, at a fixed CCl_4 flow rate of 100 sccm and a fixed V/III ratio of 64. Within measurement error, there was no apparent dependence of carrier concentration upon growth rate at a fixed V/III ratio over the range of 667–1333 Å/min.

Figure 2 shows the carrier concentration as a function of CCl_4 flow at two different growth temperatures and V/III ratios. Clearly, the carrier concentration may be controlled within a wide range by varying the CCl_4 flow between 25 and 150 sccm. A flow rate of 150 sccm represents the maximum flow rate allowed by the mass flow controller.

Figure 3 demonstrates the doping abruptness obtainable with CCl_4, as well as the lack of dopant memory effects. A lightly doped layer was grown between successively heavier doped layers at a growth temperature of 640 °C and a constant V/III ratio of 38. The CCl_4 flow variation is shown in Fig. 3(a). Each lightly doped layer had the same CCl_4 flow, and as shown in Fig. 3(b), the lightly doped layer returns to the same carrier concentration with each iteration. The polaron profile demonstrates the abruptness of the doping profiles for both the turn-on and turn-off sides of the heavily doped layers. The apparent spreading of the profile beyond a depth of 4 μm is believed to be due to nonuniformity of the etch depth after deep profiling. To further verify the doping abruptness, secondary-ion mass spectroscopy (SIMS) was used to measure the variation of carbon concentration as a function of depth in this sample. Figure 3(c) confirms that the carbon level is abrupt for the turn-on and turn-off sides of the heavily doped layers. The carbon level is also shown to increase with increasing CCl_4 flow.

Hall-effect measurements were made on a C-doped epitaxial layer that was 3 μm thick and grown on a semi-insulating substrate. The layer was grown at 640 °C and a V/III ratio of 64. A CCl_4 flow of 100 sccm was used. The hole concentration was 1.3×10^{18} cm^{-3} at 300 K and the mobility was 172 cm^2/V s at a temperature of 300 K, and 194 cm^2/V s at 77 K. The 300 K carrier concentration of this layer measured by polaron electrochemical capacitance-voltage profiling was 1.3×10^{18} cm^{-3} throughout the entire 3 μm.

The morphology of the layers grown for this study was specular, and consistent with undoped layers grown within the same time period. No molecular sieve or eutectic metal

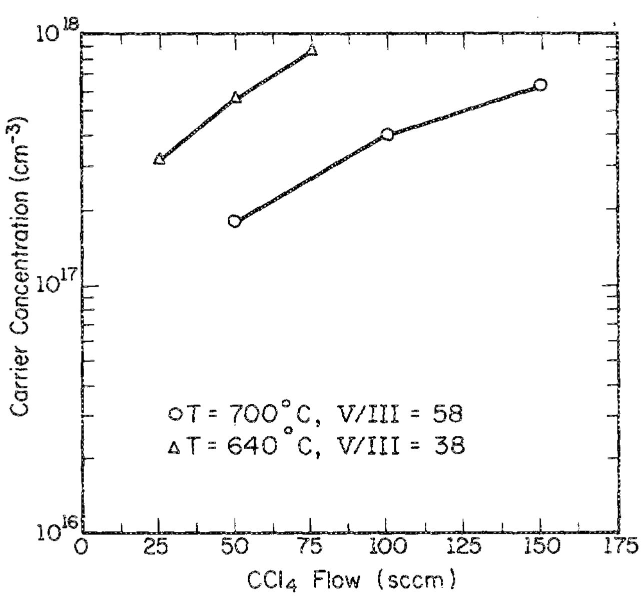

FIG. 2. Variation of carrier concentration with CCl_4 flow at two different growth temperatures and V/III ratios, and a growth rate of 2200 Å/min. Carrier concentration is controllable within a wide range by the dopant flow alone.

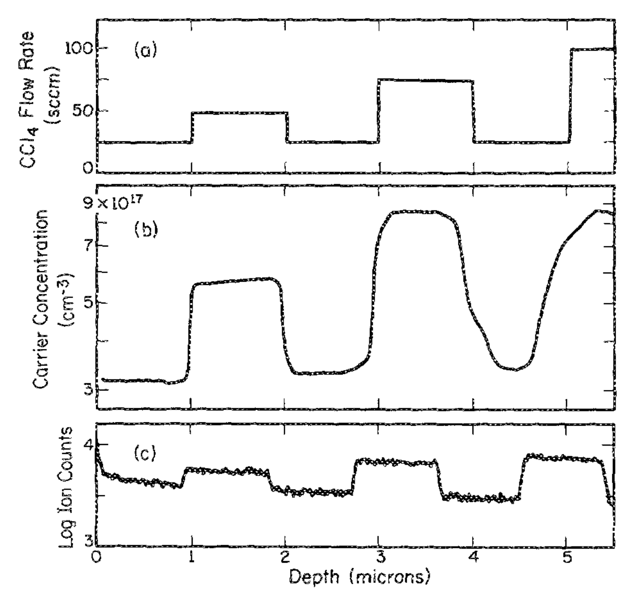

FIG. 3. Alternate lightly and heavily doped layers with the CCl_4 flow as shown in (a). The polaron electrochemical capacitance-voltage profile in (b) demonstrates abrupt turn-on and turn-off characteristics without memory effects from layer to layer. The doping abruptness has been verified by the SIMS profile of (c).

getter was utilized to remove water vapor from the CCl_4/H_2 mixture before it was introduced to the growth chamber. There was some concern about the possibility of HCl or Cl_2 formation as a side reaction to the cracking of CCl_4, which could have possible detrimental effects on the stainless-steel reactor, copper gaskets, and pump components. The very low CCl_4 concentration in the tank, combined with the heavy H_2 flow used during growth are believed to keep the possible HCl and Cl_2 concentrations at insignificant levels. No leaks formed within any part of the reactor or associated stainless-steel tubing for the duration of the experiment or any time following the experiment. During routine reactor cleaning, no apparent damage of any stainless-steel parts or copper gaskets was evident upon visual inspection.

In summary, heavy *p*-type doping of low-pressure MOCVD-grown GaAs was obtained using CCl_4. Carrier concentrations ranging between 1×10^{16} and 1×10^{19} cm^{-3} were obtained with specular morphology. Even higher carbon concentrations are expected to be attainable using higher CCl_4 partial pressures. Carbon incorporation was found to depend upon the growth temperature, the V/III ratio, and the CCl_4 flow rate. Carrier concentration was found to have no significant dependence on growth rate. Carbon tetrachloride was found to yield abrupt doping profiles, with no evidence of memory effects. In addition, no damage was apparent to any part of the reactor as a result of possible HCl or Cl_2 formation.

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