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"CARBON DOPING OF COMPOUND SEMICONDUCTOR EPITAXIAL LAYERS USING CARBON TETRACHLORIDE"

FINAL REPORT

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A dilute mixture of CCl_4 in high purity H_2 has been used as a carbon dopant source for $Al_xGa_{1-x}As$ grown by low pressure metalorganic chemical vapor deposition (MOCVD). To understand the mechanism for carbon incorporation from CCl_4 doping, and to provide experimental parameters for the growth of carbon doped device structures, the effect of various crystal growth parameters on CCl_4 doping have been studied, including growth temperature, growth rate, V/III ratio, Al composition, and CCl_4 flow rate. Although CCl_4 is an effective p-type dopant for MOCVD $Al_xGa_{1-x}As$, injection of CCl_4 into the reactor during growth of InP resulted in no change in the carrier concentration or carbon concentration from undoped InP layers.

Abrupt, heavy carbon doping spikes in GaAs have been obtained using CCl_4 without a dopant memory effect. By annealing samples with carbon doping spikes grown within undoped, n-type, and p-type GaAs, the carbon diffusion coefficient in GaAs at 825°C has been estimated and has been found to depend strongly on the GaAs background doping.

CCl_4 doping has been used in the base region of an Npn AlGaAs/GaAs heterojunction

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bipolar transistor (HBT). HBTs with 3 x 10 m self-aligned emitter fingers have been fabricated which exhibit a current gain cutoff frequency of f_t = 26 GHz.

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<u>Final Report</u>

Heavily doped p-type layers in GaAs and $Al_xGa_{1-x}As$ are commonly used in several device structures. They are important in diode lasers and in the base region of heterojunction bipolar transistors (HBTs). 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 adsorbtion of these reactants on the internal surfaces of the growth chamber and gas lines. 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. Carbon is expected to incorporate only as a shallow acceptor on an As site with very little interstitial incorporation, even at high doping levels. As a result, carbon is expected to have greatly improved diffusion characteristics in comparison to Mg and Zn.

High carbon concentrations have been obtained in GaAs grown by several techniques. High carbon acceptor concentrations have been achieved in GaAs grown by molecular beam epitaxy (MBE) using carbon evaporated from a heated graphite source. Carbon incorporation from trimethylgallium (TMGa), a common Ga growth precursor, has been used to obtain high carbon concentrations in GaAs grown by atomic layer epitaxy (ALE) and metalorganic molecular beam epitaxy (MOMBE).

Several methods for carbon doping have also been proposed for the MOCVD growth technique. Intentional addition of carbon using a number of hydrocarbon sources has not been successful, or has led to films of low carbon content. One researcher has successfully added carbon to GaAs layers with trimethylarsenic. In this work, CCl_4 is used to controllably obtain p-type GaAs and $Al_xGa_{1-x}As$ with carrier concentrations between $1x10^{16}cm^{-3}$ and $1x10^{19}cm^{-3}$ in low pressure MOCVD-grown layers. In addition, CCl_4 doping yields excellent doping abruptness and does not display the memory effects apparent with Mg and Zn doping.

First, a mixture of 500 ppm CCl_4 in H_2 was used to grow heavily doped p-type GaAs by low pressure MOCVD with TMGa and AsH_3 as the group III and V sources, respectively. Carbon acceptor concentrations between $1 \times 10^{16} cm^{-3}$ and $1 \times 10^{19} cm^{-3}$ 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 upon CCl_4 flow, V/III ratio, and growth temperature.

Next, to understand the effect of growth parameters on carbon incorporation in CCl_4 doped $Al_xGa_{1-x}As$, carbon acceptor concentration was studied as a function of Al composition, growth temperature, growth rate, and CCl_4 flow rate using electrochemical capacitance-voltage profiling. The carbon incorporation as a function of Al composition, growth temperature and CCl_4 flow rate was also measured by secondary ion mass spectroscopy (SIMS). All layers were grown by low pressure MOCVD using TMGa and TMAl as column III precursors, and 100% AsH_3 as the column V source. Increased Al composition reduced the dependence of carbon concentration on the growth temperature. Reduced growth rate, which resulted in substantially decreased carbon acceptor concentrations in GaAs, had an insignificant effect on the carrier concentration of $Al_{0.4}Ga_{0.6}As$. A linear relationship between hole concentration and CCl_4 flow rate in $Al_xGa_{1-x}As$ for $0.0 \leq x \leq 0.8$ was observed. These results indicate that adsorption and desorption of CCl_4 on the $Al_xGa_{1-x}As$ surface during crystal growth plays an important role in the carbon incorporation mechanism.

Intentional carbon doping of low pressure MOCVD grown InP was attempted with a 500 ppm mixture of $^{13}CCl_4$ in high purity H_2, which was used to obtain carbon acceptor concentrations as high as 1×10^{19} cm^{-3} in GaAs. Under growth conditions similar to those used for heavy carbon incorporation in GaAs, injection of $^{13}CCl_4$ into the growth reactor during growth of InP did not produce any measurable change in the carrier concentration of the InP epitaxial layers or any change in the ^{13}C concentration above the ^{13}C background in SIMS analysis. These results support previous low temperature photoluminescence (PL) measurements of high purity InP in which no residual carbon acceptor is observed regardless of the growth technique or conditions, and the hypothesis that carbon is not incorporated in InP grown by any epitaxial technique.

The effects of background doping, surface encapsulation, and arsenic vapor pressure on the diffusion rate of carbon in GaAs were studied by performing anneals on 1000 Å carbon-doped spikes of GaAs grown within 1 μm layers of undoped, Mg doped, and Se doped GaAs. The layers were grown by low pressure MOCVD, and CCl_4 was used as the carbon doping source for the doping spikes. The As_4 vapor pressure during annealing was controlled by the addition of elemental As to the sealed quartz ampoule used for the diffusion. For each As_4 overpressure, two samples, one Si_3N_4-capped, and one capless were annealed together. All anneals were performed at 825°C for 24 hours. SIMS was used to measure the variation of the carbon concentration as a function of depth for both the as-grown and the annealed samples. The diffusion rate of carbon is found to depend strongly upon the species used for the background doping, being highest in Mg-doped GaAs, and lowest in Se-doped GaAs. The type of surface encapsulation and the As vapor pressure are found to have a very minor effect on the carbon diffusion rate.

Finally, CCl_4 was used as a carbon doping source for the base region of a GaAs/AlGaAs Npn heterojunction bipolar transistor (HBT) grown by low pressure MOCVD. Transistors were fabricated and characterized for dc current gain, emitter-base junction ideality factor, base contact resistance, and external base resistance. Microwave characterization by S-parameter measurement was performed to determine the common emitter current gain and maximum available gain as a function of frequency. Transistors with the base contact area self-aligned to a 3 x 10 μm emitter finger had a dc current gain as high 50, an emitter-base junction ideality factor of n = 1.2, and a current gain cutoff frequency of f_t = 26 GHz. Transistors of equal emitter area without self-alignment exhibited dc current gain as high as 86, n = 1.2, and f_t = 20 GHz. A base contact resistance of $R_c = 2.85 \times 10^{-6}\ \Omega\ cm^2$, and an external base sheet resistance of R_s = 533.4 Ω/square were measured. These preliminary results indicate that carbon doping from CCl_4 may be an attractive substitute for Zn or Mg in GaAs/AlGaAs HBT structures grown by MOCVD.