Carbon doping in molecular beam epitaxy of GaAs from a heated graphite filament

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Carbon doping of GaAs grown by molecular beam epitaxy has been obtained for the first time by use of a heated graphite filament. Controlled carbon acceptor concentrations over the range of 10^{17}–10^{20} cm^{-3} were achieved by resistively heating a graphite filament with a direct current power supply. Capacitance-voltage, *p/n* junction, and secondary-ion mass spectrometry measurements indicate that there is negligible diffusion of carbon during growth and with post-growth rapid thermal annealing. Carbon was used for *p*-type doping in the base of *Npn* AlGaAs/GaAs heterojunction bipolar transistors. Current gains greater than 100 and near-ideal emitter heterojunctions were obtained in transistors with a carbon base doping of 1×10^{19} cm^{-3}. These preliminary results indicate that carbon doping from a solid graphite source may be an attractive substitute for beryllium which is known to have a relatively high diffusion coefficient in GaAs.

Carbon is well known to be shallow acceptor impurity in GaAs. Carbon is often found as a trace impurity in GaAs epilayers grown by various techniques including molecular beam epitaxy (MBE). Typical carbon background levels in MBE-grown GaAs of around 10^{14} cm^{-3} and below can be detected by sensitive measurement[1] techniques such as photoluminescence. Carbon has often been regarded as a problem in GaAs since high background levels can degrade electron mobilities by enhanced ionized impurity scattering in modulation-doped heterojunctions and also can result in thermal conversion of semi-insulating substrates to *p* type after furnace annealing. However, it recently has been recognized that carbon has many favorable properties which make it attractive for *p*-type doping in GaAs. It has a relatively small ionization energy (~ 20 meV), high solid solubility ($> 10^{20}$ cm^{-3}), and has been reported to have an extremely low diffusion coefficient in GaAs.[2] This latter property is very important since it has been shown that the conventional MBE acceptor dopant beryllium exhibits significant diffusion and surface segregation at doping levels above 1×10^{19} cm^{-3}.[3,3-5] There have been several reports of intentional carbon doping of GaAs epilayers by use of the metalorganic gas sources, trimethylgallium (TMG), and trimethylaluminum (TMAl). Carbon has been incorporated in GaAs grown by metalorganic MBE[6] and atomic layer epitaxy[2] using TMG and TMAl through incomplete cracking of the metal — carbon bonds during epitaxy. Carbon has also been used to dope $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ cladding layers *p* type in GaAs quantum well lasers grown by atmospheric pressure metalorganic chemical vapor deposition under appropriate growth conditions.[7]

In this letter, we report on the first successful carbon doping of GaAs layers grown by molecular beam epitaxy by use of a resistively heated graphite filament. Carbon doping levels up to 1×10^{20} cm^{-3} have been obtained and carbon exhibits negligible diffusion during growth and with post-growth rapid thermal annealing. An AlGaAs/GaAs heterojunction bipolar transistor with a 1×10^{19} cm^{-3} carbon-doped base operated with current gains greater than 100. The graphite carbon source has several advantages over metalorganic gas sources for carbon doping in terms of simplicity, reproducibility, independence of doping level with GaAs growth rate, and substrate orientation. Also unlike Be, TMG, and TMAl, graphite is not toxic. In addition, the simple construction of the graphite doping source saves the considerable expense of an effusion cell and pyrolytic boron nitride crucible normally used for Be doping. This initial work indicates that near ideal acceptor doping profiles with essentially no diffusion can be obtained in GaAs grown by MBE using carbon evaporated from a heated graphite source.

The graphite filaments used in this study were machined from a rectangular sheet of POCO DFP-2 grade high-purity graphite.[8] The graphite filaments were cut in a serpentine shape to yield a resistance of approximately 1 Ω and an effective evaporation area of around 1 cm^2. The filament was clamped on both ends using flat tantalum tabs attached to tantalum rods which in turn are fastened to a dual current vacuum feedthrough. The graphite filament source to substrate separation is 15 cm. The design of the graphite filament was accomplished so that only a very small fractional change in the thickness of the graphite filament occurred due to carbon evaporation for a typical growth experiment. The fractional increase in the resistance of a new filament after a typical growth run (GaAs layer doped 5×10^{19} cm^{-3}, 0.1 μm thickness) was estimated to be $\Delta R/R < 10^{-3}$. Thus the graphite filament yields reproducible doping levels over many growth experiments without the need for frequent recalibrations.

The evaporation rate of carbon from the graphite filament is determined by its temperature which is controlled by the power dissipation through adjustment of the filament current. The relation between the hole carrier concentration versus filament current as determined by van der Pauw measurements is shown in Fig. 1. It is seen that the hole concentration ranges from about 4×10^{17} to 5×10^{19} cm^{-3} at a GaAs growth rate of 1 μm/h. Hole concentrations above 1×10^{20} cm^{-3} have been obtained by employing reduced GaAs growth rates below 1 μm/h. Experimentally it has been found that the hole carrier concentration is very repro-

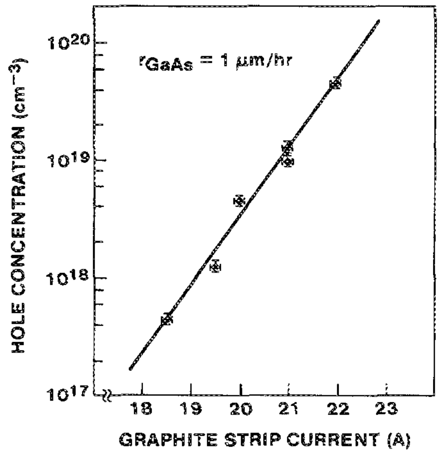

FIG. 1. Hole carrier concentration vs graphite filament current as determined by van der Pauw measurements.

ducible by setting the graphite filament current which is measured and regulated using a feedback controller which is interfaced with a computer. The 300 K hole mobility of the epilayers as a function of the hole concentration is shown in Fig. 2. It is seen that the hole mobilities are very comparable to those obtained for other typical acceptors used to dope GaAs such as Be and Zn. This also indicates that the crystallinity of the GaAs is good even at very high densities of carbon in the epilayers.

Secondary-ion mass spectrometry (SIMS) measurements show good agreement between the hole carrier concentration and the carbon concentration as determined by ion-implanted calibration standards of carbon in GaAs. This suggests that the carbon is evaporated predominantly as monatomic C_1 with molecular carbon species such as C_2 and C_3 at much lower levels. This also is in agreement with previous studies[9–11] of the heat of sublimation of carbon from graphite which indicates that the evaporation rate of C_1 is at least a factor of 10 times higher than either C_2 or C_3 for temperatures below 2400 K. The temperature of the graphite filament in these experiments was estimated to be about 2150 K (for a doping level of 1×10^{19} cm^{-3}) based upon the vapor pressure of carbon[12] and also by assuming power dissipation is almost entirely by blackbody radiation using the well-known Stefan–Boltzmann law: $P = A\sigma T^4$, where P is the power (W), A the radiative surface area of the filament (cm^2), σ the constant (5.67 W cm^{-2} K^{-1}), and T the absolute temperature (K).

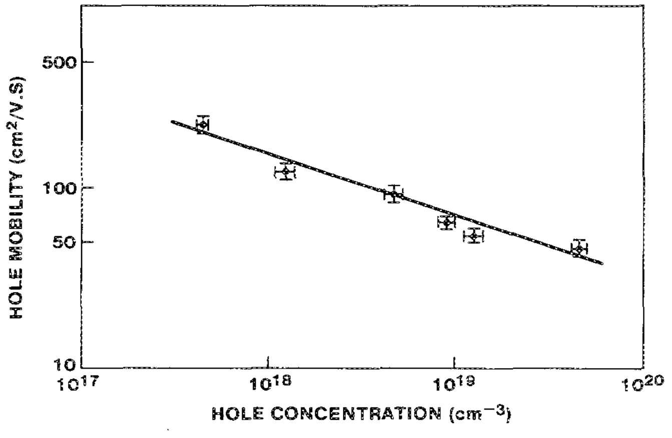

FIG. 2. Hole mobility (300 K) vs hole carrier concentration as determined by van der Pauw measurements.

The diffusion of carbon in GaAs was examined by several techniques. Secondary-ion mass spectrometry (SIMS) measurements indicated that within the resolution of SIMS (∼100 Å) there was no apparent diffusion of carbon in GaAs layers grown at 600 °C, even at doping levels as high as 5×10^{19} cm^{-3} ($Al_{0.3}Ga_{0.7}As$ layers in the structure served as markers). This is in striking contrast to the high diffusion rates and surface segregation effects observed for Be-doped GaAs grown by MBE, especially for doping levels above 1×10^{19} cm^{-3}.[3–5]

Carbon diffusion in GaAs was also examined by capacitance-voltage (*C-V*) measurements of two-dimensional doped carbon planes deposited during growth interruption by MBE. Figure 3 shows the hole carrier concentration versus distance profiles obtained by *C-V* measurements of two carbon-doped plane samples; the first as grown and the second after a 5 s 800 °C rapid thermal anneal (RTA). It is seen that both samples exhibit a full width half maximum of approximately 100 Å which is just about twice the Debye length for *p*-type GaAs doped to 1×10^{18} cm^{-3}. It is seen that there is no significant diffusion of carbon after the RTA. It is unclear at this time whether the slight tailing of the *C-V* profile for the RTA sample towards the surface is real or if it is an artifact due to slight surface roughness observed for this sample by Nomarski interference microscopy after the RTA. A more complete set of experiments is presently under way to determine quantitatively the temperature dependence of carbon diffusion in GaAs and will be reported elsewhere.[13]

Finally, an *Npn* AlGaAs/GaAs heterojunction bipolar transistor with a graded band gap base[14] was grown using

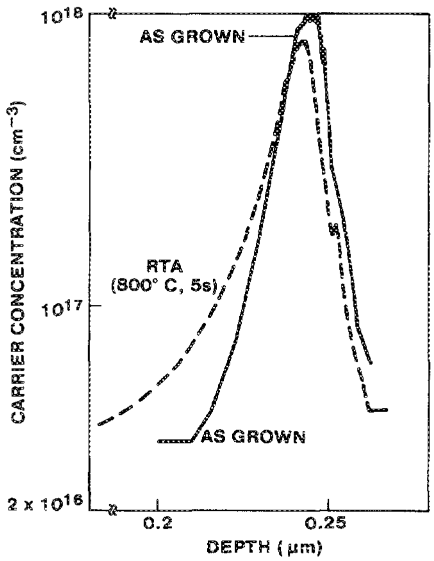

FIG. 3. Hole carrier concentration vs distance for a carbon-doped plane sample as determined from capacitance-voltage measurements. One piece of the sample was as grown and the other was rapid thermal annealed at 800 °C for 5 s before being metallized with Ti/Au Schottky contacts.

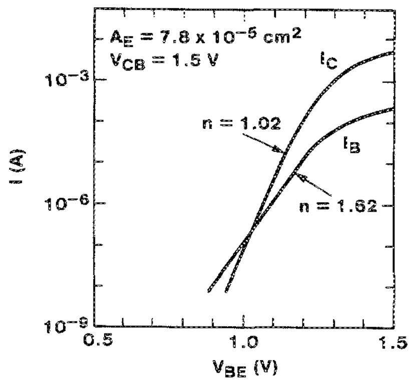

FIG. 4. Gummel plots of collector and base currents vs base-emitter voltage for a carbon-doped base *Npn* AlGaAs/GaAs heterojunction bipolar transistor measured in common-emitter configuration.

carbon for the *p*-type doping in the base. The base was doped to 1×10^{19} cm^{-3} and the Al mole fraction was graded from $x = 0$ to $x = 0.1$ over 600 Å. Both the base and the emitter ($Al_{0.3}Ga_{0.7}As$: Si, 5×10^{17} cm^{-3}) were grown at a substrate temperature of 700 °C while the collector (GaAs: Si, 5×10^{16} cm^{-3}) and emitter and collector contact layers (GaAs: Si, 5×10^{18} cm^{-3}) were grown at a substrate temperature of 600 °C. Mesa transistors were formed by chemical etching and alloying Au/Ge/Ni and Au/Be metallizations at 450 °C for the emitter/collector and base contacts, respectively. The area of the emitter mesa was approximately 7.8×10^{-5} cm^2. Figure 4 shows the Gummel plots for the collector and base currents of a test transistor measured in the common-emitter configuration. The transistors exhibit high current gain above 100 at collector current densities of several kA cm^{-2} and unity current gain at collector current densities of a few mA cm^{-2}. The emitter-base junctions are of very high quality with a measured collector current ideality factor of 1.02 and the base current ideality factor of 1.62. It is believed that the high $Al_{0.3}Ga_{0.7}As$ emitter growth temperature of 700 °C enabled by the carbon base doping contributes to the superior characteristics of the junction.

In conclusion, we have demonstrated a new and simple technique for carbon doping in GaAs grown by MBE which is based upon evaporation of carbon from a heated graphite filament. The materials quality of the carbon-doped layers is very good and there is no apparent diffusion of carbon in the layers. Carbon doping has been demonstrated in the base of *Npn* AlGaAs/GaAs heterojunction bipolar transistors in which current gains greater than 100 have been obtained at a base doping of 1×10^{19} cm^{-3}. These results indicate that carbon may be an attractive substitute for Be which is the most common acceptor dopant in MBE-grown GaAs.

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