

Carbon diffusion in undoped, n -type, and p -type GaAs

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The effects of background doping, surface encapsulation, and As_4 overpressure on carbon diffusion have been studied by annealing samples with 1000 Å p -type carbon doping spikes grown within 1 μm layers of undoped (n^-), Se-doped (n^+), and Mg-doped (p^+) GaAs. The layers were grown by low-pressure metalorganic chemical vapor deposition using CCl_4 as the carbon doping source. Two different As_4 overpressure conditions were investigated: (1) the equilibrium p_{As_4} over GaAs (no excess As), and (2) $p_{\text{As}_4} \sim 2.5$ atm. For each As_4 overpressure condition, both capless and Si_3N_4 -capped samples of the n^- , n^+ , and p^+ -GaAs crystals were annealed simultaneously (825 °C, 24 h). Secondary-ion mass spectroscopy was used to measure the atomic carbon depth profiles. The carbon diffusion coefficient is always low, but depends on the background doping, being highest in Mg-doped (p^+) GaAs and lowest in Se-doped (n^+) GaAs. The influence of surface encapsulation (Si_3N_4) and p_{As_4} on carbon diffusion is minimal.

In order to construct high-gain, high-frequency GaAs/AlGaAs heterojunction bipolar transistors (HBTs), it is necessary to grow a thin, heavily doped p -type base layer.^{1,2} For GaAs/AlGaAs HBTs grown by metalorganic chemical vapor deposition (MOCVD), the acceptor impurities Mg and Zn are commonly employed in the GaAs base layer. Unfortunately, the large diffusion coefficients associated with these impurities lead to p - n junction redistribution, either during crystal growth itself or during subsequent high-temperature processing.³⁻⁵ For example, the diffusion of Zn from the base into the n -type emitter changes the emitter-base p - n junction location relative to the emitter-base (GaAs/AlGaAs) heterojunction, thereby resulting in degraded HBT performance unless special set back doping layers are used.⁵ Recent work has identified carbon as an alternative acceptor to Mg and Zn.⁶⁻¹⁰ Because carbon incorporates primarily as a substitutional acceptor on the As sublattice (i.e., low interstitial carbon concentration), it is expected to have a much smaller diffusion coefficient than either Mg or Zn.^{6,7,11,12} A detailed understanding of carbon diffusion in GaAs and AlGaAs would be useful for the prediction of the effects of high-temperature processing on HBT and other heterolayer device performance.

In the experiments described here, the effects of background doping, surface encapsulation, and arsenic overpressure (p_{As_4}) on carbon diffusion were studied by annealing (1000 Å) p -type carbon doping spikes grown in the center of 1 μm layers of undoped (n^-), Se-doped (n^+), and Mg-doped (p^+) GaAs. Secondary-ion mass spectroscopy (SIMS) was used to measure the carbon depth profiles for both as-grown and annealed samples. In general, the carbon diffusion coefficient is found to be extremely low, but depends on the background doping. The highest carbon diffusion coefficient is observed in Mg-doped (p^+) GaAs, while little or no carbon diffusion is found in Se-doped (n^+) GaAs. The effect of GaAs surface conditions was investigated by employing Si_3N_4 encapsulation and two different As_4

overpressures. These surface conditions had only a minor influence on the carbon diffusion coefficient. Estimates for the carbon diffusion coefficient in undoped (n^-) GaAs and Mg-doped (p^+) GaAs were found by fitting a one-dimensional diffusion equation solution to the measured SIMS carbon depth profiles.

The epitaxial layers used in this work were grown by low-pressure metalorganic chemical vapor deposition (MOCVD) in an Emcore GS3100 reactor on 2° off (100) oriented liquid-encapsulated Czochralski GaAs substrates. All growths were carried out at $T_G \sim 600$ °C, $P_G \sim 100$ Torr, substrate rotation rate ~ 1500 rpm, H_2 flow rate ~ 9 slm, growth rate ~ 1000 Å/min, and V/III ratio ~ 60 . Trimethylgallium and 100% AsH_3 were the respective group III and V precursors. Nominally undoped GaAs grown under these conditions is n -type with a background carrier concentration of $n^- \sim 1 \times 10^{15}$ cm⁻³. Layers doped with Mg (p -type) using MCP_2Mg have a hole concentration of $p^+ \sim 1 \times 10^{19}$ cm⁻³ as measured by electrochemical capacitance-voltage profiling. Layers doped with Se (n -type) using hydrogen selenide have an electron concentration of $n^+ \sim 5 \times 10^{18}$ cm⁻³. All epilayers are ~ 1 μm in total thickness with the carbon doping spike (1000 Å) located 0.5 μm from the crystal surface. The carbon doping source, a 500 ppm mixture of CCl_4 in high-purity H_2 , was turned on only during the growth of the carbon doping spike. The CCl_4 flow rate for each run was sufficient for the growth conditions used to achieve a carbon acceptor concentration of $p \sim 5 \times 10^{18}$ cm⁻³.

All anneals were performed in evacuated quartz ampoules ($p \sim 10^{-6}$ Torr, vol ~ 3 cm³) at 825 °C for 24 h. For each ampoule the sample set (six samples) consisted of a capless and a Si_3N_4 -capped sample of the three as-grown crystals (n^- , n^+ , and p^+). Pyrolytic decomposition of SiH_4 and NH_3 at 700 °C was used to grow the 1000-Å-thick Si_3N_4 encapsulant. A large As_4 overpressure ($p_{\text{As}_4} \sim 2.5$ atm) was achieved by adding 25 mg of elemental As to the anneal

ampoule. For comparison, the equilibrium p_{As} over GaAs was also investigated (no excess As). The SIMS analysis for carbon was performed on the as-grown and the annealed samples using a Cameca IMS-3f instrument. The measurement conditions were 211 nA Cs⁺ primary-ion beam current (12.6 kV) and negative secondary-ion detection. High-resolution operation of the SIMS instrument was required to observe the carbon doping spike, and for this condition the detection limit for ¹²C is approximately $2 \times 10^{17} \text{ cm}^{-3}$. Any variation in carbon concentration below this limit cannot be measured.¹³⁻¹⁵

The carbon diffusion coefficient (D_c) was estimated by fitting a one-dimensional diffusion equation solution to the measured SIMS carbon profiles with the assumption that D_c is independent of the carbon concentration. The SIMS data show that the initial as-grown carbon profile is rectangular. Thus, for the annealed samples the carbon depth profiles may be expressed as

$$N(x,t) = B + \frac{N_0}{2} \left[\operatorname{erf}\left(\frac{h-x+d}{2\sqrt{D_c t}}\right) + \operatorname{erf}\left(\frac{h+x-d}{2\sqrt{D_c t}}\right) \right], \quad (1)$$

where $N(x,t)$ represents the carbon ion count as a function of depth and annealing time, N_0 is the uniform as-grown carbon count, h is the carbon spike half-width, d is the spike depth, t is the annealing time, and B is the ¹²C background. For the fits described here, $h = 500 \text{ \AA}$, $d = 5000 \text{ \AA}$, $B = 400$ ion counts, and $t = 24 \text{ h}$.

Figure 1 shows SIMS carbon profiles for undoped (n^-) GaAs both before and after annealing (825 °C, 24 h). These data indicate that carbon has diffused slightly during the 24 h annealing period. Because the ¹²C profiles for the two Si₃N₄-capped samples are independent of As₄ overpressure, we represent both by a single set of data. The data in Fig. 1 also show that carbon has diffused only slightly more in the capless annealed samples than in the Si₃N₄-capped samples. The calculated fit [Eq. (1)] is also plotted in Fig. 1 (theory) for the Si₃N₄-capped sample. The diffusion coefficient re-

quired to fit the SIMS profile is $D_c(n^-) = 1.04 \times 10^{-16} \text{ cm}^2/\text{s}$.

The SIMS profiles for Mg-doped (p^+) GaAs in Fig. 2 demonstrate that carbon has diffused to a greater degree than in undoped GaAs. As for the undoped GaAs samples, the two Si₃N₄-capped p^+ samples (no As, + As) show similar SIMS carbon profiles. Also the ¹²C profiles for the two capless annealed samples (no As, + As) are nearly identical to those for the Si₃N₄-capped samples. The theoretical carbon diffusion profile is also shown in Fig. 2 (dashed line) for the Si₃N₄-capped sample. In this case the diffusion coefficient is $D_c(p^+) = 2.34 \times 10^{-16} \text{ cm}^2/\text{s}$.

In contrast to the SIMS data for the n^- and p^+ GaAs samples, the ¹²C profiles for Se-doped (n^+) GaAs in Fig. 3 show little or no carbon diffusion during the 24 h annealing period. Because the degree of carbon diffusion is not measurable, it has not been possible to estimate D_c (825 °C) for Se-doped (n^+) GaAs.

Because carbon substitutes for As (not Ga) on the anion (not cation) sublattice, the diffusion mechanics are different from the interstitial-substitutional model that describes column II acceptor (Zn, Be) diffusion. A brief literature survey suggests that the diffusion coefficients reported here for carbon are significantly lower than for Zn [$D_{Zn}(800 \text{ °C}) \sim 6 \times 10^{-14} \text{ cm}^2/\text{s}$] and Be [$D_{Be}(800 \text{ °C}) \sim 1 \times 10^{-15} \text{ cm}^2/\text{s}$].^{3,16} A comprehensive model for carbon diffusion must account for (1) the low diffusivity, (2) the minimal influence of annealing conditions, and (3) the strong background doping dependence demonstrated in this work. If we assume that carbon interstitials (C_i) and arsenic vacancies (V_{As}) are singly ionized donors, the combination of low diffusivity, ($C_i^+ - V_{As}^-$) Coulombic repulsion, and ($C_{As}^- - V_{As}^+$) attraction suggests a V_{As} -limited diffusion mechanism.¹⁷ Since the data presented here show that carbon diffusion is independent of annealing conditions, we propose that the V_{As} for diffusion are incorporated during crystal growth (not during annealing). This viewpoint is supported by the low V_{As} diffusion coefficient

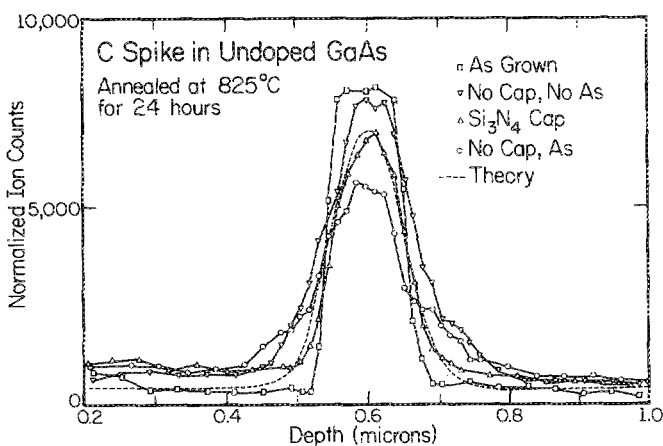


FIG. 1. SIMS depth profiles before and after annealing (825 °C, 24 h) for carbon doping spikes buried within undoped (n^-) GaAs. For the annealed samples, carbon diffusion is minimal, and is relatively independent of annealing conditions. Also shown is a solution of the one-dimensional diffusion equation [Eq. (1)] with $D_c(n^-) = 1.04 \times 10^{-16} \text{ cm}^2/\text{s}$.

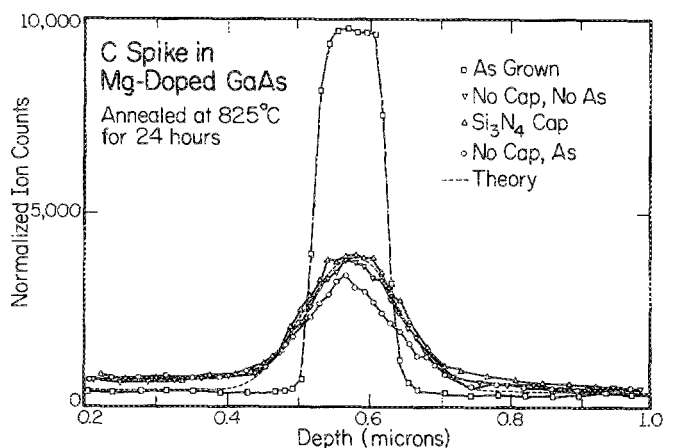


FIG. 2. SIMS depth profiles before and after annealing (825 °C, 24 h) for carbon doping spikes buried within Mg-doped (p^+) GaAs. For the annealed samples, carbon diffusion is greater than for undoped GaAs, and again is relatively independent of annealing conditions. Also shown is a solution of the one-dimensional diffusion equation [Eq. (1)] with $D_c(p^+) = 2.34 \times 10^{-16} \text{ cm}^2/\text{s}$.

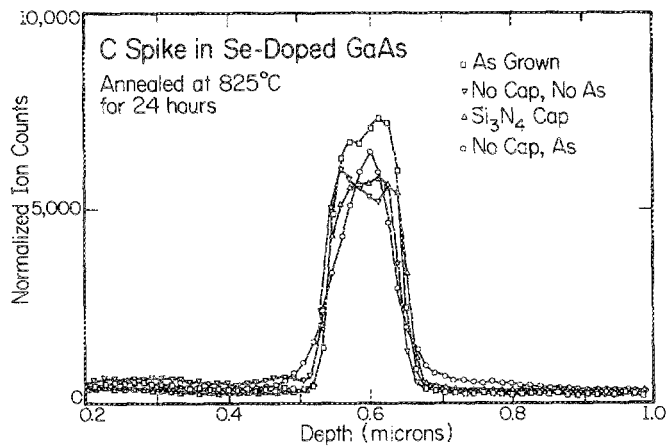


FIG. 3. SIMS depth profiles before and after annealing (825 °C, 24 h) for carbon doping spikes buried within Se-doped (n^+) GaAs. The extent of carbon diffusion is not measurable for samples annealed under various surface encapsulation and As_4 overpressure conditions.

cient at the annealing temperature [for a surface V_{As} source $< 1\%$ of V_{As} (surface) reaches a depth of $\sim 0.36 \mu\text{m}$ during an 825 °C, 24 h anneal].¹⁸

The strong background doping dependence of carbon diffusion may be attributed to the Fermi-level effect on V_{As}^+ incorporation, or to electric field-enhanced diffusion. Following the argument proposed by Valenta and Ramasastry to explain self-diffusion in Ge,¹⁹ we assume that carbon diffusion is proportional to the V_{As} concentration and that D_c is given by

$$D_c(p^+)/D_c(n^+) = [V_{As}]_{p^+} / [V_{As}]_{n^+}, \quad (2)$$

where $[]$ denotes concentration, and the p^+ (n^+) subscript refers to the Mg-doped (undoped) sample. The undoped GaAs sample is nearly intrinsic at the growth temperature with $n^- \sim 9.5 \times 10^{15} \text{ cm}^{-3}$ and $n_i \sim 9.1 \times 10^{15} \text{ cm}^{-3}$; therefore, $D_c(n^-) \sim D_c(i)$ and $[V_{As}]_{n^-} \sim [V_{As}]_i$. By applying nondegenerate Fermi-Dirac statistics to Eq. (2) after Reiss²⁰ we find

$$D_c(p^+)/D_c(i) = p^+/n_i. \quad (3)$$

In the experiments described here, the ratio p^+/n_i at the growth temperature is large (~ 1000), but the measured carbon diffusion coefficient ratio is only ~ 2.3 . This large discrepancy may be caused by the nonequilibrium crystal growth conditions, and by the inadequacy of the nondegeneracy approximation.

An alternative explanation for the background doping dependence is that the diffusing species is positively charged and is influenced by the built-in potential (V_{bi}) at the $p(C)-p^+$ (Mg), $p(C)-n^-$, and $p(C)-n^+$ (Se) junctions. The negligible potential barrier at the $p(C)-p^+$ (Mg) junction is polarized to enhance positive ion diffusion away from the carbon spike. The potential barrier for the $p(C)-n^-$ junction opposes positive ion diffusion, but is probably much smaller than the estimated value of V_{bi} (825 °C) ~ 0.42 eV because the corresponding depletion width is too large ($\sim 15 \mu\text{m}$). In contrast, V_{bi} (825 °C) for the $p(C)-n^+$ (Se) junction is large (~ 0.74 eV) and opposes positive ion diffusion. These trends are in general agreement with the observed dependence of carbon diffusion on background doping.

In summary, the effects of background doping, surface encapsulation, and As_4 overpressure on carbon diffusion were investigated by annealing samples with (1000 Å) p -type carbon doping spikes grown in the middle of $1 \mu\text{m}$ layers of undoped (n^-), Se-doped (n^+), and Mg-doped (p^+) GaAs. SIMS carbon depth profiles reveal that carbon diffusion is dependent on the GaAs background doping, but is always low. The carbon diffusion coefficient at 825 °C, determined by fitting a solution of the one-dimensional diffusion equation to the measured SIMS carbon profile, is $D_c(p^+) = 2.34 \times 10^{-16} \text{ cm}^2/\text{s}$ for Mg-doped GaAs and $D_c(n^-) = 1.04 \times 10^{-16} \text{ cm}^2/\text{s}$ for undoped GaAs. Little or no carbon diffusion is observed in Se-doped (n^+) GaAs. Both surface encapsulation and the effect of As_4 overpressure on the carbon diffusion were insignificant. These data suggest that carbon diffuses through the As sublattice via As vacancies. However, the measured background doping enhancement of carbon diffusion ($p^+ > n^- \gg n^+$) is much smaller than the calculated Fermi-level-dependent $[V_{As}]$ ratio. If the diffusing carbon species is positively charged, the background doping dependence can be explained by electric field-enhanced diffusion. Further experiments are required to identify the specific carbon diffusion mechanism.

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