Zinc delta doping of GaAs by organometallic vapor phase epitaxy

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Zinc delta-doped layers have been grown by atmospheric pressure organometallic vapor phase epitaxy. Secondary-ion mass spectroscopy and electrochemical capacitance-voltage profiling were used to measure the spatial distribution of the Zn for both as-grown and annealed samples. The narrowest atomic profiles had full width at half maxima of 70 Å for peak Zn concentrations of $\leqslant 3\times10^{18}$ cm^{-3}. The as-grown width of these profiles is attributed to a combination of dopant memory effect and growth-related diffusion during the actual formation of the delta-doped layer. An effective diffusion coefficient D of $\leqslant 7\times10^{-17}$ cm^2/s is estimated for a growth temperature of 625 °C. Rapid thermal annealing at 900 °C for 5 s of several samples grown under various conditions led to calculated values of D in the range 0.5–1.0$\times10^{-12}$ cm^2/s.

The spatial confinement of dopants to an atomic plane during epitaxial growth, so-called delta doping,[1–4] has attracted considerable attention since the first demonstration by Wood *et al.*[1] Delta doping and subsequent annealing can provide insight into the diffusion of dopants in semiconductors.[5–8] Previous work has primarily focused on the atomic diffusion of Si in delta-doped epitaxial GaAs layers grown by molecular beam epitaxy or chemical beam epitaxy.[5–7] Carbon, which is a particularly promising p-type dopant for III-V semiconductors due to its low diffusion coefficient ($\leqslant 10^{-16}$ cm^2/s at 800 °C), has also been studied.[8]

In this letter we report our results on zinc delta-doped structures in GaAs grown by organometallic vapor phase epitaxy (OMVPE). Zinc is a widely used p-type dopant in many device structures grown by OMVPE. Based on vapor phase diffusion studies of Zn into GaAs which utilize an "infinite" Zn diffusion source, relatively high diffusion coefficients (D) are found.[9] This would suggest a rather limited usefulness for Zn in device structures such as heterojunction bipolar transistors (HBTs), which have a small tolerance for diffusion into adjacent layers. However, some degree of success has been demonstrated in OMVPE-grown HBTs with Zn-doped base layers.[10,11] Recent studies of Zn diffusion in as-grown structures examined by secondary-ion mass spectroscopy (SIMS) have provided evidence that the effective Zn diffusion coefficients are several orders of magnitude smaller than "infinite" source diffusion values.[12] This may be related to the relative ratio of substitutional to interstitial Zn for the two sets of diffusion conditions. Whereas the previous report has focused on Zn diffusion in relatively thick doped layers ($\sim$1000 Å) subjected to long ($\sim$4 h) furnace anneals,[12] we have examined the diffusion from delta-doped layers subjected to rapid thermal annealing (RTA). The diffusion kinetics are expected to be somewhat different in these two cases and shorter anneal times of thin, highly-doped layers are of more relevance with respect to device fabrication steps. The limiting of Zn to several atomic planes in a buried layer also reduces effects such as dopant segregation, precipitation, and surface-related phenomena.

All of the Zn delta-doped GaAs layers were grown in a barrel-type OMVPE reactor operated at atmospheric pressure. Ultrahigh purity helium was used as the carrier gas. Trimethylgallium (TMG), diethylzinc (DEZn), and arsine were employed as the source reagents. Growth temperatures of 575–625 °C were utilized. Mole fraction ratios of AsH_3 to TMG were varied from 37 to 174. For the majority of the growth runs, the growth rate was 260 Å min^{-1}. Typically, 2000 Å of GaAs were deposited on (100) or 2° off (100) oriented p^+ and semi-insulating GaAs substrates. The delta-doped layer was then formed as follows. First, the TMG was switched to the vent line, stopping growth for 10 s. This was followed by introducing the DEZn for durations of 5–60 s, and then switching back to vent, allowing 10 s before resuming growth of an additional 1000 Å. Multiple delta-doped layers were also grown in a similar fashion.

The results obtained from the electrochemical capacitance-voltage (EC-V) profiling of a multiple delta-doped sample are given in Fig. 1. A growth temperature of 625 °C, a V/III ratio of 37, and a growth rate of 260 Å min^{-1} were used. Delta-doping took place every 1000 Å with pulse durations of 5, 15, 30, and 60 s. Maximum hole concentrations P_{max} of 2.3×10^{17} cm^{-3} at 950 Å, 9.6×10^{17} cm^{-3} at 1930 Å, 2.8×10^{18} cm^{-3} at 2950 Å, and 2.5×10^{18} cm^{-3} at 3880 Å were determined. As expected, P_{max} increased with longer pulse durations and reached a saturation value of $\leqslant 3\times10^{18}$ cm^{-3} for this particular growth temperature. While not studied in detail, it is suggested that P_{max} is limited by the vapor pressure of Zn or $ZnAs_x$ species on the GaAs surface. Furthermore, the length of time allowed to purge the DEZn from the reactor should also effect P_{max}, since this may allow evaporation of the dopant species from the surface.

A multiple delta-doped sample with four identical pulse durations of 15 s was also grown. Other growth conditions were the same as those of the previous sample. The results from SIMS and EC-V profiling are presented in Fig. 2. From the EC-V results, P_{max} values of 1.3, 0.82, 1.2, and 1.0×10^{18} cm^{-3} at 960, 1970, 3020, and 4080 Å, respectively, were obtained. The full width at half maximum (FWHM) of each

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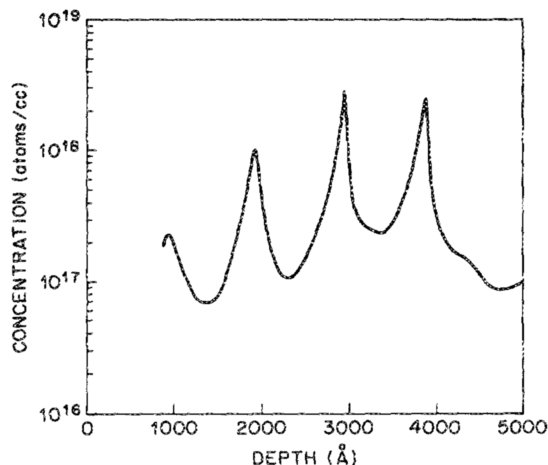

FIG. 1. Electrochemical capacitance-voltage profile of a multiple Zn delta-doped sample with pulse durations of 5, 15, 30, and 60 s.

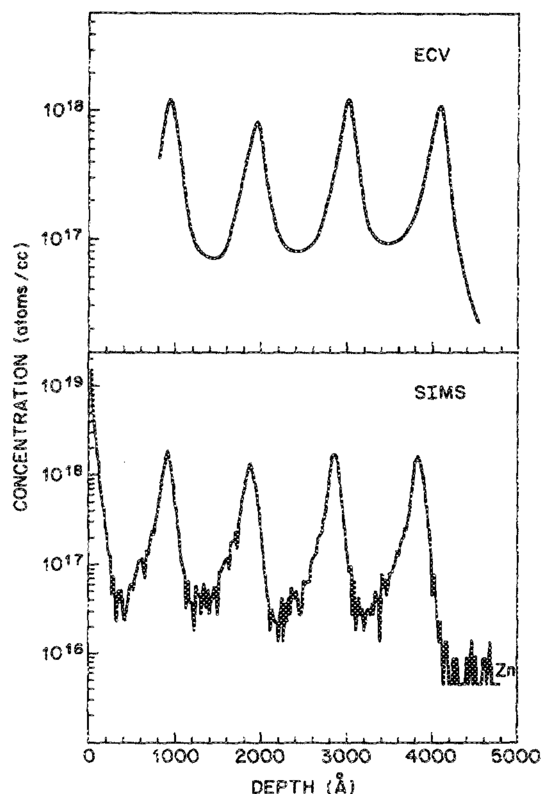

FIG. 2. Electrochemical capacitance-voltage (top) and SIMS (bottom) profiles for a multiple delta-doped sample with four identical pulse durations of 15 s.

peak was 150, 205, 160, and 170 Å, respectively. To be noted is the similar FWHM and P_{max} of each peak within the experimental error associated with the measurements and the growth conditions. These results can be compared with the SIMS data, where maximum values of total Zn concentration of 1.8, 1.4, 1.8, and 1.8×10^{18} cm^{-3} at 930, 1860, 2860, and 3800 Å were obtained, in good agreement with the electrical results. The FWHM of each peak is nearly identical at 70, 80, 70, and 70 Å, respectively. Concentration scales for the SIMS data were obtained from comparison with ion-implanted standards run under the same profiling conditions. The depth scales were obtained from direct stylus profilometry of the sputtered SIMS crater. The difference in the absolute magnitudes of P_{max} and FWHM between the SIMS and EC-V measurements is due to Debye broadening occurring for the low Zn concentration on the sides of the EC-V carrier peaks. Consequently, the SIMS values are assumed to represent the upper limit of the diffusion during growth. Since the instrumental resolution of the SIMS was $\leqslant 30$ Å, the Zn dopant atoms are seen to be limited to a few atomic planes. The SIMS and EC-V results are consistent in that negligible diffusion occurs after the formation of the delta-doped layers. An estimate of the upper limit to the diffusion coefficient will be presented below.

The FWHM of the as-grown peaks include contributions from several factors such as diffusion during subsequent growth, the dopant memory effect, and segregation of the dopant. It is also possible that diffusion can be enhanced while exposing the GaAs surface to the dopant or during the initial stages of growth of the top layer. An indication of these effects can be seen in the half width at half maximum (HWHM) for the leading and trailing slopes of the peaks. In Fig. 2, the average HWHM of the four peaks in the EC-V profile on the trailing side was 75 Å while that on the leading side was 95 Å. A memory effect, whereby the dopant desorbs from the reactor walls after termination of the Zn pulse, could explain this asymmetry. Consequently, in order to study bulk diffusion it is necessary to anneal as-grown samples and to examine the broadening of the FWHM. The mean penetration depth of the diffusant can be defined as the difference in the HWHM of the annealed and as-grown samples.[13] The effective diffusion coefficient D can be related to the mean penetration depth Z by $D=(Z/2)^2\pi/t$, where t is the annealing time.[14] Presented in Fig. 3 are SIMS profiles for a single delta-doped layer annealed at temperatures of 700, 800, 900, or 950 °C for 5 s using proximity annealing in a SiC-coated graphite susceptor within a RTA system. A pulse duration during growth of 60 s was used with other conditions remaining the same as for the previously discussed samples. The FWHM of the annealed samples were 150, 210, 530, and 540 Å and the maximum Zn concentrations Zn_{max} were 5.5, 2.4, 1.2, and 0.8, respectively. A FWHM of 100 Å and a Zn_{max} of 2.2×10^{18} cm^{-3} were obtained for the as-grown sample. The results are fairly consistent except that the as-grown Zn_{max} is somewhat lower than expected while for the 700 °C annealed sample it is larger in value. The apparent variation in Zn peak position may be related to small nonuniformities in the overlayer thickness or to variations in the sputter rate during the SIMS profiling. This has been observed previously[13] and is currently under investigation. Calculation of D for diffusion times of 5 s at the respective temperatures yields 9.8×10^{-15} cm^2/s (700 °C), 4.7×10^{-14} cm^2/s (800 °C), 7.3×10^{-13} cm^2/s (900 °C), and 7.6×10^{-13} cm^2/s (950 °C). No correction has been made for the effective diffusion times in the RTA apparatus since this would require knowledge of the activation energy for the diffusion process. However, assuming this energy is ~2.0 eV, a reasonable estimate for a substitutional diffusant in GaAs, and knowing the heating rate of 170 °C s^{-1} and cooling rate of 90 °C s^{-1} from the annealing temperature to

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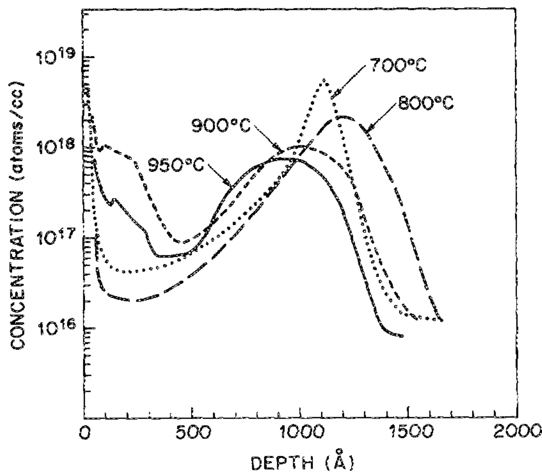

FIG. 3. SIMS profiles for delta-doped samples annealed at 700, 800, 900, and 950 °C, respectively.

500 °C, we can estimate that the D values are accurate to $\pm 12\%$.

An estimate of the maximum value of D at the growth temperature of 625 °C for the as-grown sample can be obtained by considering the delta-doped layer nearest to the substrate in the multiple delta-doped sample of Fig. 2. This layer was exposed to the growth temperature for ~ 1000 s. Assuming an uncertainty in the HWHM of the SIMS measurement as $\leqslant 30$ Å, a value for D of 7×10^{-17} cm^2/s is calculated. The actual value may well be below this estimate to the upper limit. This especially low value of the as-grown delta-doped layer is consistent with recent results by Kuech *et al.*[15] These authors have calculated values of $\leqslant 5\times 10^{-18}$ cm^2/s at 700 °C for Zn concentrations $\leqslant 10^{19}$ cm^{-3}. Our value is less than that estimated by Enquist *et al.*[12] Based on their values for D_0 and E_A of 1.0×10^{-9} cm^2/s and 0.9 eV, respectively, a value for D of 9×10^{-15} cm^2/s at 625 °C is estimated. However, the experimental conditions of these authors were different from ours and emphasize the sensitivity of Zn diffusivity in GaAs to parameters such as interstitial and substitutional Zn concentration, the doping level and conductivity type of adjacent layers, and the method of annealing.

Several additional samples were grown at various V/III ratios, growth rates, growth temperatures, and Zn_{max} values and annealed at 900 °C for 5 s. For a sample with $T_G = 600$ °C, V/III = 73, and $G = 260$ Å min^{-1}, Zn_{max} was found to be 4×10^{18} cm^{-3} by SIMS. The FWHM for the as-grown and annealed samples were 120 and 550 Å, respectively, resulting in a calculated value of $D = 7.3\times 10^{-13}$ cm^2/s. For a further sample with $T_G = 575$ °C, V/III = 174, and $G = 130$ Å/min, Zn_{max} was found to be 6.5×10^{18} cm^{-3} with a FWHM of 100 Å. The annealed sample had a FWHM of 480 Å, resulting in a calculated value of $D = 5.7\times 10^{-13}$ cm^2/s. From these results we do not see large differences in D despite the varied growth conditions.

In summary, we have demonstrated Zn delta-doped layers grown by OMVPE. The narrowest profiles had a FWHM of 70 Å for Zn_{max} of $\leqslant 3\times 10^{18}$ cm^{-3}. The as-grown width of these profiles is most likely due to a combination of dopant memory effect and growth-related diffusion during the actual formation of the delta-doped layer. An effective diffusion coefficient D of $\leqslant 7\times 10^{-17}$ cm^2/s is estimated for $T_G = 625$ °C. Rapid thermal annealing at 900 °C for 5 s of several samples grown under various conditions led to calculated values of $D \sim 0.5$–1.0×10^{-12} cm^2/s.

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