Diffusion of atomic silicon in gallium arsenide

E. F. Schubert
AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974
J. B. Stark
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
T. H. Chiu and B. Tell
AT&T Bell Laboratories, Holmdel, New Jersey 07733

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Silicon impurities with an initial Dirac-delta-function-like distribution profile are diffused into GaAs using rapid thermal annealing. The diffusion of atomic Si is determined by a novel method of comparing experimental capacitance-voltage profiles with a corresponding self-consistent profile calculation. Capacitance-voltage profiles broaden from 30 to 137 Å upon rapid thermal annealing at 1000 °C for 5 s. The diffusion coefficient and the activation energy of atomic Si diffusion in GaAs are determined to be $D_0 = 4\times10^{-4}$ cm^2/s and $E_a = 2.45$ eV, respectively. The diffusion coefficient is two orders of magnitude smaller as compared to Si-pair diffusion in GaAs.

In this letter we investigate diffusion of individual Si atoms in GaAs using rapid thermal annealing (RTA). The nonannealed GaAs layers have a Dirac-delta- function-like[1] doping profile. The diffusion is determined from electronic characteristics of the semiconductor using the capacitance-voltage profiling technique. The redistribution of Si impurities is assumed to be Gaussian and is modeled with self-consistent calculations. This technique is very sensitive and allows us to determine diffusion on a 10 Å scale. The technique is therefore well suited to diffusion determination of elements with a *small* diffusion coefficient such as Si in GaAs.

Although diffusion parameters of many elements in GaAs have been determined,[2] the diffusion coefficient and activation energy of atomic Si have not been previously determined by conventional techniques due to the very low diffusivity.[2] In contrast, the diffusion coefficient of Si pairs or Si complexes has been determined by Greiner and Gibbons.[3] They presumed that paired Si atoms have a higher diffusivity than single Si atoms due to conservation of charge and vacancy type during substitutional diffusion.[3] Omura *et al.*[4] determined the temperature dependence of the diffusion coefficient of Si pairs in GaAs under excess As pressure and obtained results comparable to those found in Ref. 3.

The epitaxial GaAs layers used for this study have been grown on n^+-type GaAs substrates in a Riber CBE32 chemical beam epitaxy system using $Ga(C_2H_5)_3$ and thermally decomposed AsH_3 for cations and anions, respectively. The substrate temperature during growth was 550 °C. The residual background concentration of undoped GaAs is p type with $N_A + N_D > 10^{15}$ cm^{-3}. The layer sequence is shown in Fig. 1 and consists of the n^+-type substrate, 9000 Å undoped GaAs, the δ-doped layer with a sheet concentration of 4×10^{12} cm^{-2}, and an undoped 1000-Å-thick GaAs top layer. After the growth process, the samples were cleaved into several pieces and the individual pieces were then annealed in an AG-Associates Heatpulse AG-410 rapid thermal annealing furnace for 5 s at temperatures ranging from 600 to 1000 °C. The time of 5 s is the actual time which the sample is exposed to the high annealing temperature.[5] AuGe/Ni/Au (2000 Å/500 Å/2000 Å) metallization has been alloyed at 420 °C for 30 s and was used for ohmic backside contacts. Circular Ti/Au (500 Å/1500 Å) Schottky contacts with a diameter of 500 μm were evaporated through a shadow mask. The capacitance-voltage (C-V) characteristics were measured on a Hewlett–Packard 4194A impedance gain-phase analyzer. The current-voltage phase angle was $> 87°$ at a frequency of 1 MHz, indicating the dominating capacitive character of the Schottky contacts. C-V concentration versus depth profiles were obtained from C-V curves using well-known equations. Additional current-voltage characteristics yielded a good ideality factor of $n = 1.04$.

Self-consistent solutions of Schrödinger's and Poisson's equations are used to obtain subband structure and charge distribution of the δ-doped semiconductor at a given Schottky voltage. An example for the subband structure of δ-doped GaAs is shown in Fig. 2. At a dopant sheet concentration of $N_D^{2D} = 5\times10^{12}$ cm^2 four eigenvalues E_0–E_3 are

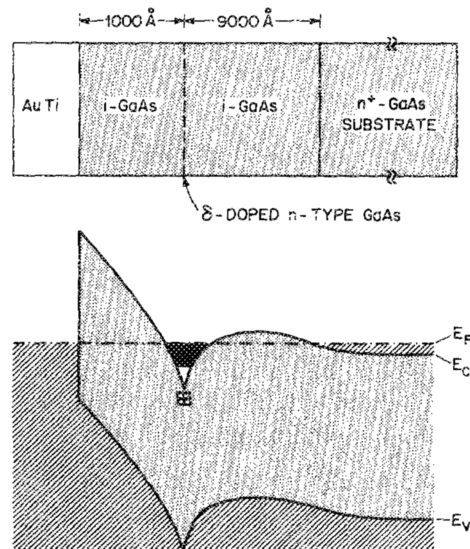

FIG. 1. Schematic layer sequence (top) of a δ-doped GaAs sample grown on a n^+-type substrate and (bottom) corresponding band diagram.

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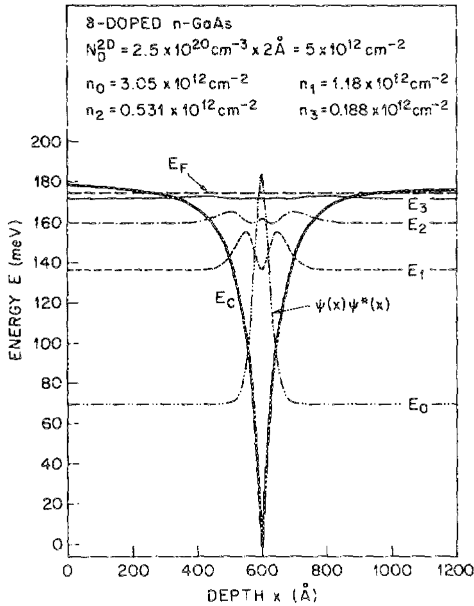

FIG. 2. Self-consistently calculated subband structure of δ-doped GaAs with a sheet dopant concentration of 5×10^{12} cm^{-2} and a Gaussian impurity distribution ($\sigma = 1$ Å).

obtained below the Fermi level. The wave functions displayed in Fig. 2 are normalized so that the product $\psi(x)\psi^*(x)$ indicates the actual population of the subbands. Many-body effects have not been taken into account in our present calculation. They are, however, not significant in the high concentration regime, due to the high kinetic energy of carriers as compared to the average interaction energy.[6] Furthermore, we assumed a parabolic dispersion relation of the $\Gamma_{2'}$, conduction-band minimum, with no significant changes of the results as compared to a nonparabolic dispersion relation.[1] Self-consistent solutions are obtained for different bias conditions (typically 15) and one specific diffusion length. Thus, theoretical charge-voltage and capacitance-voltage relationships are established, which in turn allow us to calculate theoretical *C-V* profiles.

Theoretical analysis of diffusion of Si impurities in δ-doped GaAs samples is straightforward. We assume an initial distribution according to the Dirac-delta function:

$$N_D(x) = N_D^{2D}\delta(x - x_0) \tag{1}$$

and obtain a Gaussian distribution with diffusion length $L_D = \sqrt{D\tau}$ after diffusion:

$$N_D(x) = N_D^{2D}(4\pi D\tau)^{-1/2}\exp\left(-\frac{(x-x_0)^2}{4D\tau}\right). \tag{2}$$

This normal distribution represents a solution of the one-dimensional Fickian diffusion equation. The diffusion time is denoted as τ and D is the so-called diffusion coefficient, which depends on temperature according to

$$D = D_0 \exp(-E_a/kT), \tag{3}$$

where E_a is the activation energy of the diffusion process, k is Boltzmann's constant, and T the absolute temperature. The set of equations given above is valid only for atomic diffusion but not for Si-pair or Si-complex diffusion observed previously.[3,4] Because the mean impurity separation in our δ-doped samples is approximately $[N_D^{2D}]^{-1/2} \cong 50$ Å, Si-pair diffusion is very unlikely. Furthermore, Si-cluster formation during growth (Volmer–Weber growth) is unlikely. Such a cluster formation (Si-Si bonds) would result in autocompensation and a reduction of free carriers, which is not observed experimentally. A capacitance-voltage (*C-V*) profile obtained from a δ-doped GaAs sample measured at 300 K is shown in Fig. 3. The *C-V* profile peak occurs at a depth of 1123 Å, which is in good agreement with the depth of 1000 Å anticipated during crystal growth. The full width at half-maximum of the profile is 30 Å, which is one of the narrowest *C-V* profiles measured on any semiconductor structure.[7] The narrow profile clearly demonstrates that diffusion is not important at a growth temperature of 550 °C, in agreement with our earlier results.[1] The free-carrier concentration can be obtained by integration of the *C-V* profile, as indicated by the shaded area in Fig. 3. The integral yields a density of carriers in the two-dimensional electron gas of

$$n_{2DEG} = \int N_{CV}\,dx = 4.1\times10^{12}\ \text{cm}^{-2},$$

in good agreement with the anticipated value.[8] After annealing samples at temperatures ranging from 600 to 1000 °C for 5 s, the shape of the *C-V* profiles changes drastically, as shown in Fig. 4. The full width at half-maximum increases from 30 Å for the as-grown sample up to 137 Å for the sample annealed at 1000 °C. Furthermore, the maximum *C-V* concentration drops from $\geqslant 7\times10^{18}$ cm^{-3} for the as-grown sample to $\leqslant 3\times10^{18}$ cm^{-3} for the sample annealed at 1000 °C. The free-carrier concentration (integral of *C-V* profile) decreases by about 10% from 4.1×10^{12} cm^{-2} to 3.7×10^{12} cm^{-2}. This minor reduction suggests that some Si impurities might have diffused on As vacancies, i.e., acceptor sites.

The actual diffusion lengths and diffusion coefficients can be obtained from the *C-V* profiles using two approaches. First, calculated *C-V* profiles, assuming Gaussian diffusion profiles of different L_D, are compared with measured *C-V*

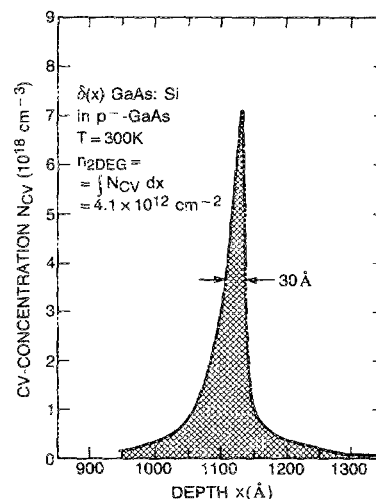

FIG. 3. Capacitance-voltage profile of a δ-doped GaAs sample. Integration of the profile yields the sheet free-carrier concentration of $n_{2DEG} = 4.1\times10^{12}$ cm^{-2}.

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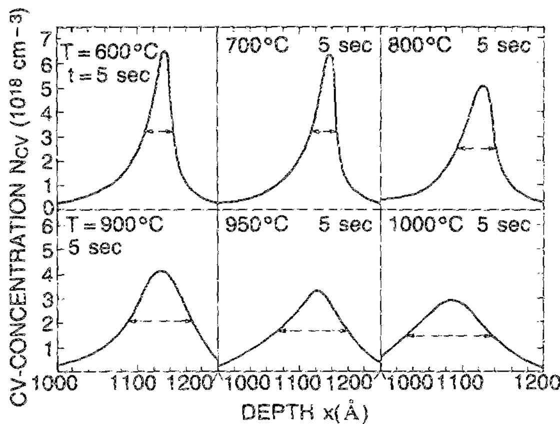

FIG. 4. C-V profiles of different pieces of a δ-doped GaAs sample rapidly thermally annealed at temperatures $600\,^{\circ}\mathrm{C} \leqslant T \leqslant 1000\,^{\circ}\mathrm{C}$ for 5 s.

profiles. From this comparison the appropriate diffusion length, valid at one specific annealing temperature, is inferred. For this method, the background doping type and concentration of the semiconductor is required, because C-V profile widths depend (weakly) on background doping. A second approximate method to determine diffusion lengths and coefficients can be obtained by assuming a diffusion broadening L_D and an intrinsic broadening L_i of the C-V profiles. The total broadening is then given by[9]

$$L = (L_i^2 + L_D^2)^{1/2}. \quad (4)$$

This equation allows us to easily determine a diffusion length from a C-V profile. This second method yields good results for initially narrow nonannealed profiles, as shown in Fig. 3. For large L, self-consistent calculations are required to determine L_D.

The diffusion coefficients, which are determined from the diffusion lengths according to $D = L_D^2/\tau$, are shown versus reciprocal temperature in Fig. 5. The activation energy of the diffusion process determined from the Arrhenius plot is $E_a = 2.45$ eV. The extrapolated diffusion coefficient for $T \rightarrow \infty$ is $D_0 = 4 \times 10^{-4}$ cm^2/s. The diffusion coefficient found in this study is extremely small as compared to other impurities in III-V semiconductors.[2] Furthermore, the diffusion coefficients depicted in Fig. 5 are two orders of magnitude smaller than the diffusion coefficients obtained for Si-pair diffusion[3,4] in GaAs. Ths finding is in agreement with a presumption of Greiner and Gibbons,[3] who expected a larger diffusion coefficient for Si complexes in GaAs. The diffusion mechanism is presumably substitutional diffusion on Ga sites since both interstitial diffusion and diffusion via As vacancies, i.e., acceptor sites, would result in a significant reduction of the free-carrier concentration which we do not observe. Furthermore, our diffusion coefficient at $T = 850\,^{\circ}\mathrm{C}$ of $D = 4 \times 10^{-15}$ cm^2/s is in excellent agreement with diffusion data of Si ion-implanted GaAs.[10]

Our findings allow an estimate of Si diffusion during growth of δ-doped samples by molecular beam epitaxy at a growth temperature of 550 °C. Using the results of Fig. 5 we obtain a diffusion length of only 1.2 Å, which corroborates our earlier results of insignificant diffusion during growth.[1]

In conclusion, we have examined atomic Si diffusion in GaAs. Si impurities with an initial Dirac-delta-function-like doping profile are diffused into GaAs using rapid thermal annealing. Our novel method which employs C-V profiling and self-consistent calculations is very sensitive, even to small amounts of diffusion, and the method is therefore well suited for determination of diffusion at relatively low temperatures or of elements with small diffusion coefficients. An activation energy of 2.45 eV and a diffusion coefficient of 4×10^{-4} cm^2/s are determined for atomic Si diffusion in GaAs. The diffusion coefficient of atomic Si diffusion is two orders of magnitude smaller than the diffusion coefficient of Si-pair diffusion in GaAs.

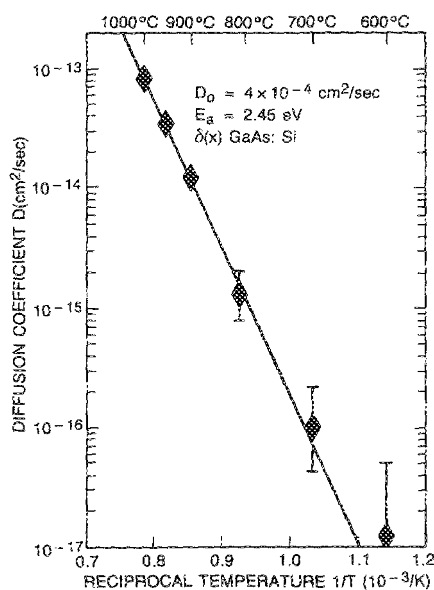

FIG. 5. Diffusion coefficient for atomic Si diffusion in δ-doped GaAs vs reciprocal temperature.

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[8] The free-carrier concentration obtained by integration of the C-V profile agrees with the value of a Hall measurement of the same epitaxial layer grown side by side on a semi-insulating GaAs substrate.
[9] It is necessary to differentiate between the full width at half-maximum and the standard deviation of a Gaussian probability distribution. The full width at half-maximum equals 2.36 times the standard deviation. For a 30-Å-wide C-V profile the intrinsic broadening is determined to be $\sigma = \sqrt{2}L_i = \sqrt{2D\tau} = 13$ Å.
[10] Diffusion coefficients for Si in GaAs at $T = 850\,^{\circ}\mathrm{C}$ have been summarized by M. E. Greiner and J. F. Gibbons, J. Appl. Phys. **57**, 5181 (1985). The diffusion coefficients range from 1×10^{-15} to 2×10^{-14} cm^2/s.

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