Identification of Silicon Interstitials in Ion Implanted GaAs

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The lattice location and diffusion of silicon has been studied in [100] GaAs implanted with 1×10^{16} 40-keV $^{30}Si^+$ ions/cm^2. The identification of silicon interstitials was made by fitting a concentration dependent diffusion model to the annealed silicon depth profiles measured with secondary ion mass spectrometry. In the diffusion model presented, in addition to silicon located on Ga and As sites and Si_{Ga}^+-Si_{As}^- pairs, interstitial silicon is also taken into account for the first time. The charge state of the silicon interstitial was calculated to be +1 in order to best fit the experimental profiles. [S0031-9007(98)06688-5]

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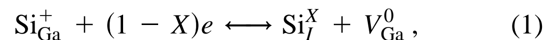
The determination of lattice location and charge state of impurities in semiconductors is of fundamental interest and important in designing device structures. As the main n-type dopant, an experimental study of the lattice location of silicon in GaAs has been made by Bhattacharya *et al.* [1], where particle induced x-ray emission (PIXE) measurements revealed that about 30% of the implanted Si atoms, after annealing, are interstitials. Extensive theoretical and experimental studies of Si diffusion in GaAs have been made [2–5]. Yu *et al.* [4] developed a Fermi level dependent diffusion model, where Si diffuses through Ga and As vacancies. At low concentrations, Si is assumed to occupy Ga sites, making the material n-type, while at higher Si concentrations compensation will occur and the active donor concentration saturates at about 2×10^{19} cm^{-3} [6]. This compensation effect mainly results because Si is a group-IV amphoteric impurity and also occupies As sites, where it acts as an acceptor. In a previous study of Si diffusion in GaAs, we showed the need to include the effect of Si interstitials in the diffusion process to explain the experimentally observed depth profiles [5]. In this Letter, a new diffusion model taking these interstitials into account is presented. The results show that the charge state of silicon interstitials in GaAs is +1 and that the As vacancies do not play an important role in the redistribution of atoms in GaAs.

Commercially prepared samples of undoped, single crystal GaAs were implanted by 40-keV $^{30}Si^+$ ions to total fluences of 1×10^{16} atoms/cm^2, where the [100] crystal axis was tilted 7° off the beam direction to avoid channeling. The annealings were carried out in a quartz-tube furnace in Ar atmosphere at a pressure of 660 torr. During the annealings at 750 °C for 2 h and at 850 °C for 30 min, the samples were encapsulated by GaAs wafers to minimize impurity buildup on the GaAs surface and the possible loss of arsenic. The experimental Si depth profiles were measured with secondary ion mass spectrometry (SIMS), as described elsewhere [5].

The diffusion model described below assumes that Si diffuses as atomic interstitials and via Ga vacancies, which are the most abundant point defects in n-type GaAs [7]. The equilibrium reaction between Si on Ga and interstitial sites is



$$Si_{Ga}^+ + (1 - X)e \longleftrightarrow Si_I^X + V_{Ga}^0 , \qquad (1)$$

where Si_I^X is a Si interstitial with charge state X, V_{Ga}^0 is a neutral Ga vacancy, and e is an electron. From this reaction, we get the relation for the Si_{Ga}^+ and Si_I^X concentrations, denoted by the square brackets

$$\frac{[Si_{Ga}]n^{1-X}}{[V_{Ga}^0][Si_I]} = K_I , \qquad (2)$$

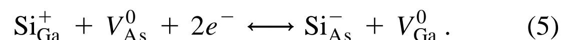
where n is the electron concentration and K_I is the equilibrium constant. Writing

$$K_I[V_{Ga}^0] = B , \qquad (3)$$

Eq. (2) becomes

$$\frac{[Si_{Ga}]n^{1-X}}{[Si_I]} = B , \qquad (4)$$

where the parameter B determines the relative amount of Si on Ga sites to interstitials. The simplest chemical reaction describing the changeover process between Si_{Ga}^+ and Si_{As}^- is



$$Si_{Ga}^+ + V_{As}^0 + 2e^- \longleftrightarrow Si_{As}^- + V_{Ga}^0 . \qquad (5)$$

From this reaction we get the relation between the concentrations of Si_{Ga}^+ and Si_{As}^-,

$$\frac{n^2[Si_{Ga}]}{[Si_{As}]} = K , \qquad (6)$$

where K is defined as the vacancy fraction constant

$$K = \frac{k[V_{Ga}^0]}{[V_{As}^0]} . \qquad (7)$$

The total Si concentration is

$$C_t = [Si_{Ga}] + [Si_{As}] + [Si_I] . \qquad (8)$$

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The charge neutrality in GaAs is

$$n + [\mathrm{Si}_{\mathrm{As}}^-] = p + [\mathrm{Si}_{\mathrm{Ga}}^+] + X[\mathrm{Si}_I], \tag{9}$$

where $p = n_i^2/n$ is the hole concentration and n_i is the intrinsic electron concentration. From Eqs. (4)–(9), the total Si concentration C_t as a function of the electron concentration can be written as

$$C_t = \frac{(n_i^2/n - n)(1 + n^2 + n^{1-X}/B)}{n^2/K - 1 - n^{1-X}X/B}. \tag{10}$$

In addition to isolated $\mathrm{Si}_{\mathrm{Ga}}^+$ and $\mathrm{Si}_{\mathrm{As}}^-$, $\mathrm{Si}_{\mathrm{Ga}}^+$-$\mathrm{Si}_{\mathrm{As}}^-$ pairs also exist. The total Si concentration can now be written as

$$C_t = [\mathrm{Si}'_{\mathrm{Ga}}] + [\mathrm{Si}'_{\mathrm{As}}] + 2[\mathrm{Si}_p] + [\mathrm{Si}_I], \tag{11}$$

where the concentrations of isolated Si on Ga and As sites are

$$\begin{aligned}[\mathrm{Si}'_{\mathrm{Ga}}] &= [\mathrm{Si}_{\mathrm{Ga}}] - [\mathrm{Si}_p], \\ [\mathrm{Si}'_{\mathrm{As}}] &= [\mathrm{Si}_{\mathrm{As}}] - [\mathrm{Si}_p].\end{aligned} \tag{12}$$

The concentration of pairs can also be expressed by using the equilibrium reaction between substitutional silicon and silicon existing as pairs,

$$[\mathrm{Si}_p]K_p = [\mathrm{Si}'_{\mathrm{Ga}}][\mathrm{Si}'_{\mathrm{As}}], \tag{13}$$

where K_p is the pair-equilibrium constant. Solving the pair concentration from Eqs. (6), (12), and (13) gives

$$[\mathrm{Si}_p] = \frac{K_p + [\mathrm{Si}_{\mathrm{Ga}}](1+\gamma)}{2} - \frac{\sqrt{\{K_p + [\mathrm{Si}_{\mathrm{Ga}}](1+\gamma)\}^2 - 4\gamma[\mathrm{Si}_{\mathrm{Ga}}]}}{2}, \tag{14}$$

where $\gamma = n^2/K$. The flux equation for the mobile $\mathrm{Si}'_{\mathrm{Ga}}$ and Si_I is

$$D_{\mathrm{eff}} \frac{\partial C_t}{\partial x} = D_{\mathrm{SG}} \frac{\partial[\mathrm{Si}'_{\mathrm{Ga}}]}{\partial x} + D_{\mathrm{SI}} \frac{\partial[\mathrm{Si}_I]}{\partial x}, \tag{15}$$

where D_{eff} is the total effective diffusion coefficient, $D_{\mathrm{SG}} = D_{\mathrm{SG}}^0 + D_{\mathrm{SG}}^{-3}(n/n_i)^3$, D_{SG}^0 is the diffusion coefficient for Si diffusing via neutral and D_{SG}^{-3} via triply negatively charged Ga vacancies [4,5], and D_{SI} is the diffusion coefficient for interstitial silicon. The effective diffusion coefficient can be solved using Eqs. (4),(6), (11)–(15):

$$\begin{aligned}D_{\mathrm{eff}} = D_{\mathrm{SG}}\Bigg\{&\frac{\partial[\mathrm{Si}_{\mathrm{Ga}}]}{\partial C_t}\left(1 - \frac{\partial[\mathrm{Si}_p]}{\partial[\mathrm{Si}_{\mathrm{Ga}}]}\right) \\ &+ \Gamma\left[\frac{\partial[\mathrm{Si}_{\mathrm{Ga}}]}{\partial n}\left(1 - \frac{\partial[\mathrm{Si}_p]}{\partial[\mathrm{Si}_{\mathrm{Ga}}]}\right) - \frac{\partial[\mathrm{Si}_p]}{\partial n}\right]\Bigg\} \\ &+ D_{\mathrm{SI}}\left\{\frac{\partial[\mathrm{Si}_I]}{\partial C_t} + \Gamma\frac{\partial[\mathrm{Si}_I]}{\partial n}\right\},\end{aligned} \tag{16}$$

where the additional terms are

$$[\mathrm{Si}_{\mathrm{Ga}}] = C_t/\alpha, \tag{17}$$

$$\Gamma = \partial n/\partial C_t, \tag{18}$$

$$[\mathrm{Si}_I] = n^{1-X}C_t/(B \cdot \alpha), \tag{19}$$

where $\alpha = 1 + n^2/K + n^{1-X}/B$. Equation (16) was used to numerically calculate the diffusion profiles for the annealed profiles. First, the electron concentration n was calculated from Eq. (10) with some initial values for the parameters K and B. The intrinsic electron concentration n_i values used for 750 and 850 °C were 4.555×10^{16} and 0.131×10^{18} atoms/cm^3, respectively [8]. Second, Eqs. (14), (18), and (19) were used to calculate the effective diffusion coefficient from Eq. (16). The concentration dependent diffusion equation [5] was solved numerically and compared with the experimental SIMS profiles. The diffusion coefficients D_{SG}^0, D_{SG}^{-3}, and D_{SI} together with parameters K, K_p, and B were obtained by least squares fitting using different integers for the interstitial charge state X. Figure 1 shows the resulting fits when the interstitial charge state is 0, +1, and +2 for the 750 °C annealed profile. The only fit that matches the whole profile is obtained for $X = +1$. In Fig. 2, the fits to the profiles annealed at 750 and 850 °C are plotted for charge state +1. As may be noted the fits are in good agreement with the experimental profiles, and the values of the fitted diffusion parameters for these temperatures are $D_{\mathrm{SG}}^0 \approx 0.03$ and 0.18 nm^2/s, $D_{\mathrm{SG}}^{-3} \approx 3.0 \times 10^{-5}$ and 2.1×10^{-3} nm^2/s, $D_{\mathrm{SI}} \approx 0.14$ and 0.66 nm^2/s, $K \approx 13 \times 10^{36}$ and 25×10^{36} cm^{-6}, $K_p \approx 3.7 \times 10^{18}$ and 5.9×10^{18} cm^{-3}, and $B \approx 0.40 \times 10^{18}$ and 0.2×10^{18} cm^{-3}, respectively. Also, other Ga vacancy combinations were tried, but the best fits were obtained with the neutral and triply negatively charged ones. The possible effect of the implantation induced damage to the diffusion is not strong, as indicated by our previous study [5]. In that study the Rutherford backscattering spectrometry in the channeling configuration (RBS/channeling)

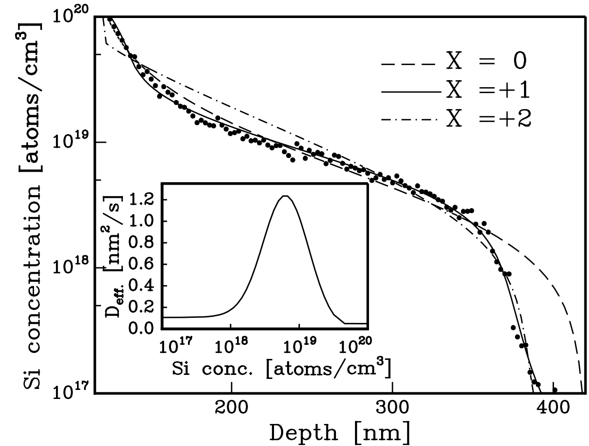

FIG. 1. The numerical fits to the 750 °C annealed profile obtained with interstitial Si charge states 0, +1, and +2. The inset shows the effective diffusion coefficient as a function of the total Si concentration for the charge state +1.

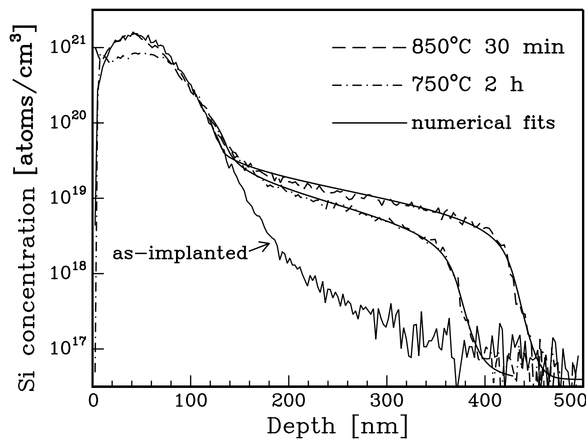

FIG. 2. The experimental SIMS profiles for samples annealed at 750 °C for 2 h and 850 °C for 30 min with the corresponding interstitial charge state +1 fits.

measurements showed that the implantation induced damage has been annealed out already at 500 °C. Figure 3 presents the theoretical electron concentration given by the present model as a function of the total Si concentration [see Eq. (10)] for the 750 and 850 °C annealings and the experimental data of Ref. [9]. In Ref. [9], Gwilliam *et al.* measured the carrier concentrations of undoped Si implanted GaAs with the differential Hall method at room temperature after annealing at 900 °C for 1000 s. Note that the theory provides the electron concentrations at the annealing temperature. In the Si concentration region $10^{16}-10^{17}$ atoms/cm^3, the electron concentration in Fig. 3 increases due to the growing number of intrinsic carriers (n_i) as a function of temperature [8].

The ratio of interstitial Si atoms to substitutional atoms has been determined by Bhattacharya and Pronko [1]. They conclude from PIXE measurements that about 30% of the Si atoms are interstitials in 120 keV, 5×10^{15} atoms/cm^2 implanted GaAs. This result can be compared with the theoretical fraction of interstitial Si atoms obtained using the present model. From Eqs. (4), (6), and (19) we get

$$F_{\text{int}}(\text{theory}) = \frac{n^{1-X}/B}{1 + n^2/K + n^{1-X}/B}. \quad (20)$$

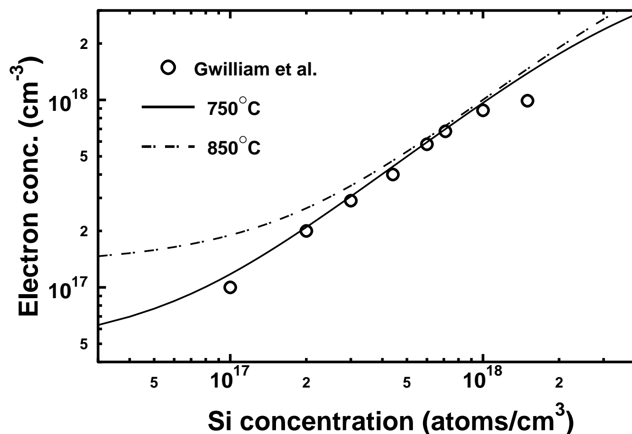

FIG. 3. Theoretical electron concentrations as a function of the total Si concentration. The experimental values of Gwilliam *et al.* [9] have been measured at room temperature after 900 °C, 1000 s annealing.

The maximum Si concentration in the experimental work by Bhattacharya and Pronko [1] is about 10^{20} atoms/cm^3, which we also use in Eq. (10) to calculate the electron concentration and further the Si interstitial fraction from Eq. (20). The result from this calculation was that at temperatures 850 and 750 °C about 42% and 38% of silicon atoms are interstitials, respectively. Although direct comparison of the theoretical interstitial fraction and electron concentrations calculated at the annealing temperature with the experimental values obtained at room temperature is not fully justified, it shows that the fitting parameter values are reasonable. Another point in favor of the present model is that, in previous silicon diffusion models [4], diffusion through As vacancies had to be included to fit the experimental results. However, according to theoretical calculations by Baraff and Schlüter [7], no As vacancies exist in n-type GaAs, where the most abundant intrinsic defect is the Ga vacancy, a fact in good agreement with the present diffusion model.

Recent work by Ashwin *et al.* [10], using infrared absorption to reveal localized vibrational modes of Si complexes, shows that Si occupies Ga and As sites and that Si_{Ga}-Si_{As} pairs exist in heavily doped GaAs. More interesting is their result of an electron trap called Si-X, which they suggest is a perturbed Si_{Ga}-V_{Ga} center but they do not rule out the possibility that the electron trap might be a defect complex involving a Si interstitial. The lattice location experiments [1] and our results show that a considerable amount of Si interstitials are present in GaAs, and the obtained +1 charge state attracts the negatively charged Ga vacancies. Hence, we suggest that the electron trap Si-X could be a complex involving a silicon interstitial.

In summary, experimentally observed interstitial silicon has been included in a concentration dependent diffusion theory. The comparison of the theoretically calculated spectra with the experimental profiles indicates that the charge state of the Si interstitials is +1.

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