Impurity Diffusion via an Intermediate Species: The B-Si System

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(Received 22 June 1990)

Motion of a substitutional impurity via a fast-diffusing intermediate species is discussed. An analytical solution is given for the case of low impurity concentration. For short times, few atoms migrate and the solution behaves exponentially. We observe this exponential signature in the diffusion of nanometer-scale B-doping profiles in Si. The migration frequency during oxidation-enhanced diffusion is consistent with diffusion-limited kickout of an interstitial-type B species. This is the first direct experimental evidence for dopant diffusion in Si via an intermediate species.

PACS numbers: 66.30.Jt

The basic mechanisms of impurity diffusion in semiconductors are the subject of considerable interest for both scientific and technological reasons. Nevertheless, many years of experimental study have so far failed to produce a firm conclusion as to the dominant mechanisms involved. Dopant diffusion experiments involving the injection of excess point defects have provided some of the best available information,¹ but even these experiments rely on somewhat uncertain theoretical assumptions and do not provide detailed information on diffusion mechanisms. One of the essential problems is that diffusion profile spreading is typically observed on a length scale that is several orders of magnitude above the atomic scale of the basic interactions.

Recently, a fundamental analysis of dopant diffusion in Si has been made with the help of quantummechanical calculations.² The energetically favored pathways for all possible diffusing species were estimated for the dopants B, P, As, and Sb. For example, for the interstitial-mediated component of diffusion, the favored pathway was the kickout reaction. In this reaction, a self-interstitial reacts with a substitutional dopant atom to form an interstitial impurity atom that migrates for some distance before recombining. Specific conclusions were also reached regarding vacancy-mediated and concerted-exchange components of diffusion.

These state-of-the-art theoretical results go far beyond the information gathered so far from experimental techniques. In a sense, this enhances their value, but it also raises doubts. The most significant overlap with experiments available to the authors of Ref. 2 was the calculated activation energy for diffusion. This does not provide a sufficient test of the predictions regarding specific mechanisms. The search for experimental methods that provide a more substantive test for theory is an issue of growing importance.

In this Letter, we report a significant step in this direction. We point out that diffusion via an intermediate migrating species, for example, the interstitial dopant atoms proposed in Ref. 2, obeys a different statistical law from diffusion via a single-jump process. Furthermore, this difference provides a signature by which such processes can be recognized experimentally. It may even prove possible to assess the absolute reaction rates for formation of the migrating species: a highly significant test of theory. We first present a brief statistical treatment of diffusion via an intermediate migrating species. We then present the results of an experiment using nanometer-scale B-doping profiles, which demonstrates the successful observation of diffusion via an intermediate species.

Two forms of the impurity, a substitutional species X_s and a migrating species X_m , are considered in our analysis. The interchange between the two forms relies on interactions with point defects present in the material. Thus, the formation of a migrating species X_m of interstitial type may consume a self-interstitial I or generate a vacancy V, according to the reactions $X_s + (1-j)I$ $\Rightarrow X_m + jV$, with j=0 or 1. For example, if X_m represents an isolated impurity interstitial, then the equation with j=0 represents the kickout reaction and the equation with j=1 represents the Frank-Turnbull dissociation reaction. Precisely analogous reactions apply to the formation of a migrating X-I pair. For a migrating X-V pair the equivalent reactions are $X_s + (1-j)V \Rightarrow X_m + jI$, with j=0 or 1.

In the case of diffusion via an interstitial-type migrating species, the reaction probabilities for $X_s \rightarrow X_m$ and $X_m \rightarrow X_s$ can be shown to be, respectively,³

$$g = g^* [(1 - \gamma)C_I / C_I^* + \gamma], \qquad (1)$$

$$r = r^* [(1 - \gamma) + \gamma C_V / C_V^*].$$
(2)

Here, C with the appropriate subscript represents the concentration of I or V, asterisks denote equilibrium quantities, and γ represents the equilibrium branching

ratio for the reaction j = 1.

If one can neglect spatial variations in the concentrations C_I and C_V in the region of interest, then g and r can be treated as constants and a simpler analysis is possible. This holds under thermodynamic equilibrium conditions in a homogeneous material. It also holds under steady-state conditions such as interstitial injection during oxide growth, provided that other localized sources and sinks of point defects are absent. In the more general case, with inhomogeneity due to high impurity concentration gradients or a heterogeneous material, numerical simulations including the reaction-diffusion equations for the point defects can be used. The following analysis, however, provides the clearest understanding of the problem and is valid for the important case of a dilute substitutional impurity in a homogeneous matrix.

In this case, the impurity transport can be described by just two equations:

$$\partial C_m / \partial t = D_m \nabla^2 C_m - r C_m + g C_s , \qquad (3)$$

$$\partial (C_s + C_m) / \partial t = D_m \nabla^2 C_m \,. \tag{4}$$

Furthermore, since we are assuming a predominantly substitutional impurity, we also have $g/r \ll 1$. One may therefore neglect the small terms $\partial C_m/\partial t$ to obtain a quasi-steady-state form for C_m in terms of C_s . A straightforward solution for $C_s(x,t)$ in one space dimension x is then possible. The solution after time t for an initial δ -function impurity profile at depth x_0 can be expressed in terms of a universal function $s(\xi, \theta)$ as

$$C_{s}(x,t) = s(\xi,\theta)\Phi/\lambda, \qquad (5)$$

where Φ is the areal density of the impurity profile (atoms/unit area), and $\xi = (x - x_0)/\lambda$ and $\theta = gt$ are dimensionless space and time variables. The quantity θ is identical to \bar{n} , the mean number of migration events per impurity atom, which determines the stochastic evolution of the solution. The quantity $\lambda = \sqrt{D_m/r}$ is the mean projected path length for the migrating species between its formation and recombination. It can be shown that the universal function $s(\xi, \theta)$ is given by⁴

$$s(\xi,\theta) = \sum_{n=0}^{\infty} P_n(\theta) f_n(\xi) , \qquad (6)$$

$$P_n(\theta) = (\theta^n/n!)e^{-\theta}, \qquad (7)$$

$$f_{n=0}(\xi) = \delta(\xi) , \qquad (8)$$

$$f_{n>0}(\xi) = [e^{-|\xi|}/2^n(n-1)!]C_n(|\xi|), \qquad (9)$$

where the C_n are polynomials defined by

$$C_n(z) = \frac{(n-1)!}{2^{n-1}} \sum_{k=0}^{n-1} \frac{2^k}{k!} {2n-2-k \choose n-1} z^k.$$
(10)

The functions $P_n(\theta)$ and $f_n(\xi)$ have a clear physical meaning. $P_n(\theta)$ is the probability for an impurity atom to have undergone *n* migration events at time *t*, and

 $f_n(\xi)$ is the spatial distribution for such atoms. The distributions for n = 0-5 are shown in Fig. 1.

For short times, $\theta = \overline{n} < 1$, the solution is given to first order by the leading terms n = 0 and 1:

$$s(\xi,\theta) = e^{-\theta} [\delta(|\xi|) + \theta e^{-|\xi|}/2] + O(\theta^2).$$
(11)

Thus, with a buried δ -doping profile, for example, impurity diffusion begins with the appearance of exponential tails on either side of a static δ -function peak. The magnitude of the exponential tails increases with time, until $\bar{n} \sim 1$ when the first-order approximation breaks down. As time increases further, the significant terms in the series of Eq. (6) shift to increasingly higher order. The solution approaches a Gaussian as \bar{n} becomes large, in accordance with the central limit theorem.

The statistical behavior we have described is intuitively evident in retrospect. Indeed, the special case $\bar{n} \ll 1$ which can be derived from a relatively simple analysis has previously been applied to the anomalous diffusion of oxygen in Si at low temperatures.⁵ However, our statistical treatment conflicts with the "common sense" usage of Fick's law which dominates most thinking about diffusion processes. It should be emphasized that Fick's law is in general inapplicable to diffusion via an inter-



FIG. 1. Probability $P_n(\theta)$ that an impurity atom has made *n* migration steps at time $t = g\theta$, and the corresponding spatial distribution $f(\xi)$ after *n* steps. The first few steps, which dominate the initial profile evolution, are shown. The universal diffusion function $s(\xi,\theta)$ for an initial δ -function profile is the sum $\sum P(\theta)f(\xi)$ over all *n*.

mediate migrating species, even when the impurity concentration is low and the system is in thermodynamic equilibrium. It fails because the flux is not purely determined by the local gradient in the substitutional impurity concentration. Only in the limit $\bar{n} \rightarrow \infty$ does Fick's law give the correct result. This assessment is of general relevance since many impurity-semiconductor diffusion systems are suspected to involve an intermediate species. In the case of a genuine single-jump diffusion process, on the other hand, Fick's law is valid.

The observation of exponential diffusion behavior at short times should provide a clear signature of diffusion via an intermediate species, provided that a sufficiently narrow initial impurity distribution can be prepared. In the rest of this Letter we describe an experimental investigation of the B-Si diffusion system, in which we show directly, for the first time, that B diffuses via an intermediate species of interstitial type. This demonstration is performed using a simple, high-resolution experiment, with a low B concentration to minimize driving forces due to the impurity gradient. B-doping spikes with a width of ~ 12 nm and a peak concentration of 2.8×10^{18} cm^{-3} were grown by molecular-beam epitaxy onto (100)-oriented Si with a 100-nm intrinsic Si buffer layer. The spikes were covered with a 55-nm Si capping layer grown at a rate of 0.2 nm/s at 550 °C. Samples were annealed at temperatures in the range 600°C (110 h) to 900 °C (5 min). Both inert and dry O₂ ambient gases were used. Annealing times were chosen to give a diffusion length $2\sqrt{Dt} \sim 10-20$ nm, large enough to detect with secondary-ion mass spectroscopy (SIMS), and potentially capable of generating exponential diffusion profiles. B depth profiles were determined by SIMS, using a CAMECA IMS-3f instrument with a 2-5-keV O₂ analyzing beam. Estimated precision of the relative SIMS yield, which determines the profile shape,



FIG. 2. Diffusion of a narrow MBE-grown B profile in oxidizing ambient at 600 °C. Solid symbols represent the asgrown profile and open symbols represent the profile after 110-h diffusion. The profile evolution is non-Gaussian. The solid line represents a convolution of the as-grown profile with the analytical function of Eqs. (5)-(10), with $\theta=0.5$ and $\lambda=10$ nm.

is better than 5%. The influence of SIMS artifacts such as recoil mixing is less than 1.5 nm/decade on the rising edge of the B profile. Neither of these effects constitutes a significant source of error in the present case.

Our results for the temperature range 600-900 °C show that B diffusion is substantially enhanced by oxidation. This is consistent with previous observations reviewed in Ref. 1. Since oxidation injects a large excess concentration of self-interstitials,¹ the data confirm that B is diffusing via an interstitial-mediated mechanism.

Results obtained for diffusion at 600 °C are shown in Fig. 2. Solid symbols represent the as-grown B profile and open symbols indicate the profile after diffusion for 110 h in O₂ ambient. Essentially no broadening is seen at the peak of the profile, while an exponential-like tail is seen on both sides of the peak. The diffused profile can be fitted very closely by convolving the as-grown B profile with the analytical distribution for an initial δ function, given by Eqs. (5)–(10). The quantities θ and λ are the fitting parameters. They are easily distinguished in the fitting procedure, because the standard deviation of the analytical distribution is given by $\lambda \sqrt{2\theta}$ while the exponential decay length is given by λ alone. The solid line represents the best fit, obtained with $\theta = \bar{n} = 0.5$ and $\lambda = 10$ nm. In contrast, Fig. 3 shows the result of convolution with a Gaussian distribution with the same variance as was used in Fig. 2. The profile so obtained is completely inconsistent with the experimental data.

The results we have described provide direct evidence that B diffuses via an intermediate migrating species. At 600 °C, this species travels a mean projected distance of ~10 nm before recombining to the substitutional form. Furthermore, the value of $\bar{n}=0.5$ implies that only ~40% of the substitutional B atoms experienced a migration event during the 110-h 600 °C anneal.

The idea of such an extremely low migration frequency might seem somewhat surprising. However, a frequency of this order of magnitude is in fact predictable if



FIG. 3. Illustration of the poor fit to the experimental data of Fig. 2 obtained with the assumption of Gaussian diffusion. The dashed line represents a convolution of the as-grown profile with a Gaussian distribution. The standard deviation is the same as in the fit of Fig. 2.

the kickout mechanism proposed in Ref. 2 is assumed. According to this proposal, we may neglect the dissociative mechanism and set $\gamma = 0$. Equations (1) and (2) reduce to $g = g^* C_l/C_l^*$ and $r = r^*$, respectively. The mean projected path length for the migrating species becomes $\lambda = \sqrt{D_m/r^*}$, independent of the point-defect conditions. Thus, the same value of λ is expected under both inert and oxidizing ambient conditions. Most significantly, the formation rate g cannot exceed the encounter rate between self-interstitials and substitutional dopant atoms. This implies an upper limit for the formation rate,⁶

$$g = 4\pi a D_{\mathrm{Si},I} C_{\mathrm{Si}} C_I / C_I^* , \qquad (12)$$

where $D_{Si,I}$ is the interstitial component of self-diffusion, *a* is the capture radius between the self-interstitial *I* and the substitutional B atom B_s, and C_{S1} is the number density of Si lattice atoms. To estimate the rate according to Eq. (12), we assume generally accepted values for $D_{Si,I}$ (Ref. 7) and for *a* (1 nm). In addition, we use our experimental data for inert- and oxidizing-ambient conditions to estimate $C_I/C_I^* \sim 10^2$ for the data shown in Fig. 2, assuming that the vacancy component of inertambient B diffusion is small. These considerations lead us to the order-of-magnitude estimate $g \sim 7 \times 10^{-7} \text{ s}^{-1}$. For our experiment this implies $\bar{n} \sim 0.3$, entirely consistent with our experimental value $\bar{n} = 0.5$.

The present work provides direct evidence that B diffuses via an intermediate species of interstitial type. In addition to its intrinsic scientific interest, this provides a physical basis for computer programs that model silicon technology processes.

The possibility of detecting diffusion via an intermediate migrating species is not restricted to the case of B in Si. Recent advances in the fabrication of nanometerscale structures may facilitate similar experiments in a number of impurity-semiconductor systems, and resolve some long-standing issues. For instance, diffusion of a substitutional impurity via an interstitial migrating species may be driven by the kickout mechanism $[\gamma=0$ in Eqs. (1) and (2)], or by the Frank-Turnbull mechanism ($\gamma=1$). In the former case, $\lambda = \sqrt{D_m/r}$ is independent of the point-defect conditions because $r \rightarrow r^*$. However, in the latter case, λ is sensitive to the vacancy concentration because $r \rightarrow r^* C_V/C_V^*$. Thus, controversies over kickout versus Frank-Turnbull mechanisms which have gone on for some years may potentially be resolved by high-resolution experiments like the one we have described.

We would like to thank C. G. Van de Walle, A. A. van Gorkum, H. F. F. Jos, and P. Zalm for useful discussions. Thanks are also due to H. Melissen and W. H. A. Schilders for discussions on the mathematics, and for finding a compact derivation of Eqs. (6)-(10).

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