Experiments on Atomic-Scale Mechanisms of Diffusion

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Many substitutional impurities in crystalline solids diffuse by a hybrid mechanism involving a fast-migrating intermediate species. Nonequilibrium measurements of the migration frequency g and migration length λ for such an impurity can provide definitive data on atomic-scale diffusion mechanisms. We report the first experimental study to exploit this approach. The system investigated is B in crystalline Si. B is shown to diffuse predominantly via a migrating interstitial species B_i, generated by a kick-out reaction. The observed mechanism and energetics agree with recent total-energy calculations.

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The atomic processes involved in solid-state diffusion at elevated temperatures are of broad scientific and technological interest. As a result, efforts have been made over the years to determine the basic mechanisms of impurity diffusion in a wide variety of systems. However, in the important case of semiconductors, the detailed mechanisms of impurity diffusion have proved extremely elusive [1]. For instance, the dominant pathways for diffusion of the common dopants in silicon have been predicted from total-energy calculations [2], but no experimental test of these detailed predictions has so far been possible. Most of what is "known" about these systems has been derived from indirect experimental evidence interpreted with the help of somewhat uncertain theoretical models.

An intriguing feature of recent theoretical results (Ref. [2]) is that almost all the common doping impurities in silicon are predicted to diffuse via a fast-diffusing intermediate species, either an impurity interstitial or an impurity-vacancy pair. In either case, diffusion is supposed to proceed by a series of migration events of frequency g as the impurity switches randomly between its more probable substitutional (immobile) form and its less probable (fast-diffusing) form. During each migration event, the impurity performs a fast random walk which terminates at some distance from the starting point when the impurity reverts to its substitutional form.

Recently, we pointed out the possibility of detecting this type of diffusive process experimentally [3]. For small diffusion times $t < 1/g$, the mean number of migration events $\bar{n} = gt < 1$. Assuming an initial δ-function impurity distribution, the one-dimensional spatial distribution at time t then takes the form

$$s(|x|/\lambda, gt) = (1-gt)\delta(x) + gte^{-|x|/\lambda} + O((gt)^2),$$

where the first term represents impurity atoms which have not yet diffused, and the second term represents atoms that have experienced a single migration event with mean projected path length λ. The space variable x represents the depth relative to the initial δ-function position. On the other hand, for longer diffusion times, $gt \gg 1$, the spatial distribution can be described using Fick's law with an average diffusivity for the impurity, $D = \lambda^2 g$. The evolution of $s(|x|/\lambda, gt)$ for all gt has been analyzed in Ref. [3] for the important case of linear diffusion. The essential point here, however, is that the exponential impurity diffusion profile predicted when $t \ll 1/g$ provides a signature by which one can recognize diffusion via an intermediate species.

The above analysis was used in Ref. [3] to explain the observation of exponential-like diffusion profiles of B in Si at high spatial resolution. For the combination of time, temperature, and ambient conditions reported (110 h at $\sim 600\,^\circ$C in dry O_2 ambient gas) values of $g \sim 1.2 \times 10^{-6}$ s^{-1} and $\lambda = 10$ nm were inferred. The large migration length, more than an order of magnitude above the elementary jump length of "normal" substitutional diffusion, provided the first clear experimental evidence of dopant impurity diffusion via an intermediate migrating species. However, it was not possible to reach a definitive conclusion on the mechanism of formation of the migrating species.

In the present Letter, we propose a new technique for determining the atomic mechanism of diffusion, which appears to be widely applicable in the solid-state field. It represents an important extension of the method presented in Ref. [3], combining the advantages of earlier point-defect injection experiments [1] with the microscopic detail obtainable when both g and λ are determined. There are only two essential requirements for applicability of the method: First, there must be an intermediate migrating species with a migration length large enough to be resolved experimentally, and second, it must be possible to vary the point-defect concentrations in the material in a predictable manner. The power of the technique is illustrated by an experimental study of the Si:B system, providing the first conclusive determination of the dominant diffusion mechanism for a dopant impurity in Si.

Consider a substitutional impurity X_s that diffuses via a fast-migrating impurity species which could be an impurity interstitial X_i or an impurity-vacancy pair X_v. There are just four possible impurity reactions involving X_i, X_v, and the self-interstitial I and vacancy V. These

are

$$X_s + I \rightleftharpoons X_i \,, \qquad (1)$$

$$X_s \rightleftharpoons X_i + V \,, \qquad (2)$$

$$X_s + V \rightleftharpoons X_v \,, \qquad (3)$$

$$X_s \rightleftharpoons X_v + I \,. \qquad (4)$$

The generation rate for X_i taking the parallel reactions (1) and (2) into account can be shown to be

$$g_{X_i} = g^*_{X_i}[(1-\gamma_V)C_I/C_I^* + \gamma_V] \,, \qquad (5)$$

where C represents the concentration of the relevant species, asterisks indicate equilibrium quantities, and γ_V is the relative probability for reaction (2) under equilibrium conditions. Likewise, as described in Ref. [3], the mean projected path length traveled before X_i recombines is given by

$$\lambda_{X_i} = (D_{X_i}/r_{X_i})^{1/2} \,, \qquad r_{X_i} = r^*_{X_i}[(1-\gamma_V) + \gamma_V C_V/C_V^*] \,, \qquad (6)$$

where r_{X_i} is the recombination rate. Identical equations to (5) and (6), with I (i) and V (v) interchanged, apply to the generation rate g_{X_v} and path length λ_{X_v} for diffusion via an impurity-vacancy pair. Thus, in the general case, both the migration frequency g and the migration length λ are sensitive to the concentrations of I and V.

To help visualize the influence of nonequilibrium conditions on the parameters g and λ, we distinguish four special cases, each corresponding to diffusion dominated by just one of the reactions (1)–(4). Table I shows the results. Each reaction exhibits its own unique response to changes in the concentrations of self-interstitials and vacancies. Thus if both g and λ can be measured, their sensitivity to point-defect injection will provide a clear signature of the predominant mechanism of diffusion.

TABLE I. Theoretical prediction of the generation rate g and migration length λ for the migrating species X_i or X_v, for four different mechanisms of diffusion.

Dominant reaction	Generation rate	Migration length
$X_s + I \rightleftharpoons X_i$	$g^*_{X_i} C_I/C_I^*$	$(D_{X_i}/r^*_{X_i})^{1/2}$
$X_s \rightleftharpoons X_i + V$	$g^*_{X_i}$	$[D_{X_i}/(r^*_{X_i} C_V/C_V^*)]^{1/2}$
$X_s + V \rightleftharpoons X_v$	$g^*_{X_v} C_V/C_V^*$	$(D_{X_v}/r^*_{X_v})^{1/2}$
$X_s \rightleftharpoons X_v + I$	$g^*_{X_v}$	$[D_{X_v}/(r^*_{X_v} C_I/C_I^*)]^{1/2}$

We now go on to describe a first application of the technique. We choose to study the Si:B system, because B is already known to exhibit exponential diffusion in Si [3], and specific state-of-the-art theoretical predictions of the B atomic diffusion mechanism are available for comparison with our observations [2]. B-doping spikes with a width of ~ 10 nm and peak concentrations of 1.2×10^{18} cm^{-3} or 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- or 120-nm Si capping layer grown at a rate of 0.2 $nm\,s^{-1}$ at 550 °C. Samples were annealed at temperatures from 600 to 900 °C for a range of times, in both inert and oxidizing ambient gases. Oxidation is known to inject self-interstitials I into the silicon [1], leading to a large increase in C_I which we use to probe the diffusion mechanism. B depth profiles were measured by secondary-ion mass spectroscopy (SIMS), according to a previously described procedure [3].

Some typical results obtained for diffusion at 625 and 900 °C are compared in Fig. 1. Solid symbols represent the as-grown B profile and open symbols indicate profiles after diffusion. A substantial difference in the shape of the diffusion profiles is apparent at the two temperatures,

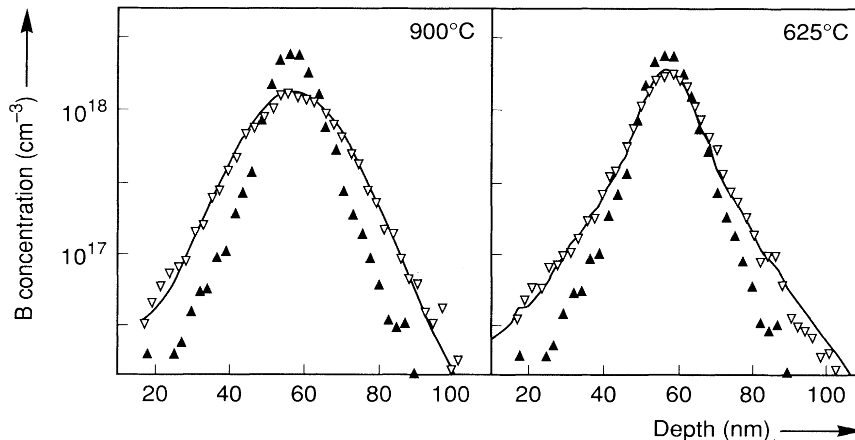

FIG. 1. Comparison of SIMS data for diffusion at 900 °C (5 min, N_2 ambient, rapid thermal anneal) and 625 °C (110 h, dry O_2 ambient). Solid symbols, molecular-beam-epitaxy–grown B profile; open symbols, profile after diffusion. Curves represent fits of the linear diffusion function $s(|x|/\lambda, gt)$ to the data.

even though the standard deviations of the profiles are nearly the same. This is possible because the shape is controlled by the value of λ, while the diffusion length is given by $2(Dt)^{1/2}=2\lambda\bar{n}^{1/2}$, where $\bar{n}=gt$ is the mean number of migration events during the anneal time t. We attribute the difference in the profile shapes to a larger migration length λ at the lower temperature. For the conditions of Fig. 1, this produces a transition from the regime $\bar{n}>1$ (Gaussian-like diffusion) at 900 °C to the regime $\bar{n}<1$ (exponential-like diffusion) at 625 °C. The solid curves in Fig. 1 are fits to the diffused profiles, obtained by convolving the as-grown B profile with the linear diffusion function $s(|x|/\lambda,gt)$ derived in Ref. [3]. We find $\lambda<5$ nm at 900 °C, but $\lambda=10$ nm at 625 °C with an uncertainty of about 1 nm. The corresponding values of $\bar{n}=gt$ are $\bar{n}>3$ for the 900 °C data and $\bar{n}=0.4$ for the 625 °C data.

Essentially identical diffusion behavior and fitted parameters are found with samples having peak B concentrations of 1.2×10^{18} cm^{-3} and 2.8×10^{18} cm^{-3}. This confirms that the B concentrations used in the present study are low enough to avoid significant composition-dependent (nonlinear) effects.

As mentioned earlier, the evolution with time from exponential to Gaussian diffusion is a characteristic feature of linear diffusion with a finite migration length. The effect is clearly illustrated by a sequence of data obtained at 700 °C in dry O_2 ambient, shown in Fig. 2. At short times, extended tails appear in the distribution with little broadening in the peak region, while at longer times the distribution appears Gaussian. The curves in Fig. 2 show the corresponding fits using a *single* value of $\lambda=6$ nm to describe the time evolution of the dopant profile for $t=3$, 10, and 30 h.

Experimental profile shapes under different ambient conditions can be directly compared by increasing the diffusion time for inert ambient conditions to produce the same diffusion length as for oxidizing ambient. The resulting diffusion profiles are found to be identical within experimental errors. For example, a diffusion for 30 h in N_2 at 700 °C produces an experimental profile that is indistinguishable from the 3-h O_2-ambient data in Fig. 2. This provides direct evidence that λ is unaffected by the ambient conditions, but that g is strongly affected (by a factor 10 in this example).

Figure 3 shows the results of an analysis in which we fit our complete set of measured profiles with the function $s(|x|/\lambda,gt)$ to extract the parameters λ and g. Circles indicate data for inert-ambient conditions, during which we expect the self-interstitial concentration to be close to equilibrium. Triangles indicate data for dry-O_2-ambient conditions, during which self-interstitials I are injected into the silicon. The data show conclusively that the injection process causes an increase in g by a factor of about 10 throughout the temperature range studied, but

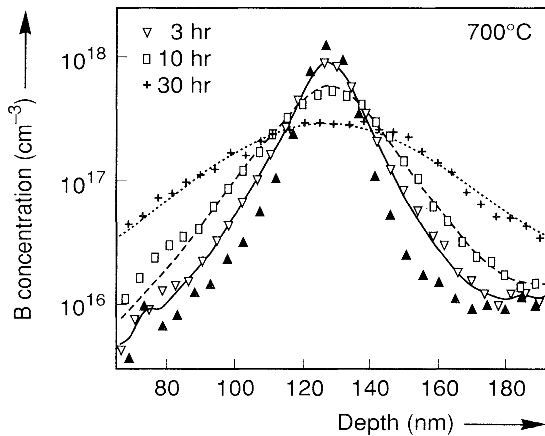

FIG. 2. Time evolution of diffusion at 700 °C in dry O_2 ambient. Symbols and curves have the same meaning as in Fig. 1. All three fitted curves were generated using $\lambda=6$ nm.

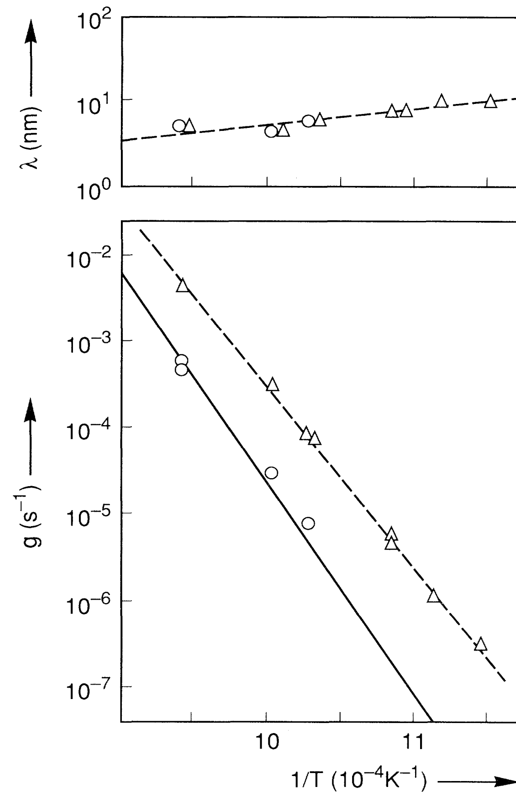

FIG. 3. Arrhenius plot of g and λ in the temperature range 800–600 °C. Circles indicate inert (N_2) ambient diffusion conditions, and triangles indicate dry O_2 ambient. Errors are comparable with the size of the symbols. The solid line is a theoretical estimate described in the text, and the dashed lines are a guide to the eye. The increase in g between N_2 and O_2 ambient conditions, together with the insensitivity of λ to the ambient conditions, is a definitive sign of a kick-out diffusion mechanism.

does not bring about any significant change in λ. Referring to Table I, it is clear that only the mechanism $B_s + I \rightleftharpoons B_i$ can produce this type of response to an increase in C_I. With this mechanism, the generation (kick-out) reaction rate increases as the number of available self-interstitials is increased, while the spontaneous recombination (kick-in) reaction that controls the value of λ is unaffected. One may therefore conclude that B diffusion in Si is dominated by a substitutional-interstitial mechanism, controlled by the kick-out reaction of Eq. (1).

The solid line in Fig. 3 represents the calculated kick-out frequency, assuming that $B_s + I \rightarrow B_i$ is a diffusion-limited reaction as described in Ref. [3]. The coincidence between the solid line and the experimental values of g for near-equilibrium diffusion conditions (circles) provides additional support for our conclusions, and indicates that any effective energy barrier to the kick-out reaction must be small (<0.3 eV) [4]. Our results confirm the qualitative conclusion from recent total-energy calculations (Ref. [2]), that a kick-out mechanism is the dominant contribution to B diffusion in Si.

A further test of theory arises from the temperature dependence of the migration length. For a kick-out mechanism, this is given by $\lambda = (D_{B_i}/r_{B_i})^{1/2}$. The activation energy for D_{B_i} is the migration energy of the B interstitial, $E_m^{B_i}$, and the activation energy for r_{B_i} is the energy barrier for the kick-in process, $E_{\text{kick-in}}^{\text{barrier}}$. Consequently, the migration length takes the form $\lambda = \lambda_0 \exp(-E_\lambda/kT)$, where $E_\lambda = (E_m^{B_i} - E_{\text{kick-in}}^{\text{barrier}})/2$ and λ_0 is a constant. In Ref. [2], values of $E_m^{B_i} \sim 0$ eV and $E_{\text{kick-in}}^{\text{barrier}} \sim 1$ eV were calculated, but could not be verified by conventional diffusion experiments. The calculated values, and their estimated uncertainties [5], imply $E_\lambda = -0.5 \pm 0.5$ eV, indicating that λ should exponentially *increase* as a function of $1/T$. Our experimental data (Fig. 3) confirm this trend. The slope of the data indicates a value of $E_\lambda = -0.4 \pm 0.2$ eV, consistent with the theory.

Finally, the kick-out rates g observed in Fig. 3 provide a basis for estimating λ for other impurities that also diffuse by the kick-out mechanism. In the case of a diffusion-limited kick-out reaction for impurity X in Si, the value of g depends purely on self-diffusion and is independent of the impurity. The value of $\lambda = (D/g)^{1/2}$ then scales with the impurity diffusion coefficient as $\lambda_X/\lambda_B = (D_X/D_B)^{1/2}$. For impurities such as Au or Pt in Si where D_X is several orders of magnitude greater than D_B, one might therefore expect values of λ approaching the micron range. This suggests the possibility of some striking experimental observations in a number of systems.

In summary, a novel technique for determining the atomic mechanism of diffusion has been proposed and demonstrated. It is valid for systems where diffusion proceeds via an intermediate migrating species. We have used the technique to obtain the first conclusive determination of a dopant diffusion mechanism in Si, including significant new data related to the reaction energy barrier. These results provide solid evidence in support of recent theory on dopant impurity diffusion in Si [2]. The same experimental approach promises definitive results for many solid-state systems where the diffusion mechanism is currently unknown or a matter of controversy.

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[4] In discussing the kick-*out* reaction, we define the effective barrier height relative to the initial configuration $(B_s + I)$ at infinite separation. For a predominantly substitutional impurity, any intermediate configuration of lower energy formed along the reaction pathway (such as the B_s-I pair discussed in Ref. [2]) will provide a reservoir of impurity atoms awaiting kick-out, but will not influence the net reaction rate g. In discussing the kick-*in* reaction, the barrier height is defined relative to the initial configuration B_i.

[5] C. S. Nichols (private communication).