

## General expression for effective diffusivity of foreign atoms migrating via a fast intermediate

Kejia Chen, Ramakrishnan Vaidyanathan, Edmund G. Seebauer, and Richard D. Braatz<sup>a)</sup>  
*University of Illinois at Urbana-Champaign, 600 South Mathews Avenue, Box C-3, Urbana, Illinois 61801, USA*

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In many solids, diffusion of foreign atoms takes place primarily through highly mobile intermediate species that periodically exchange with atoms in the crystalline lattice. The governing reaction-diffusion equations include a diffusion coefficient as well as kinetic parameters describing the exchange of the intermediate species. Yet it is often convenient to model a diffusive process in terms of a single parameter, no matter what the time regime. This communication derives for a delta function initial profile an exact expression for the effective diffusivity that is valid in all time regimes. In the case of semiconductor solids, such an expression can be helpful in the interpretation of dopant diffusion measurements. © 2010 American Institute of Physics. [doi:10.1063/1.3294479]

The diffusion of foreign atoms in crystalline solids has been studied extensively to understand the governing mechanisms and, in the case of semiconductors, to facilitate improvements in device fabrication.<sup>1</sup> In semiconductors such as silicon, studies of dopant diffusion<sup>2-4</sup> and isotopic self-diffusion<sup>2,5,6</sup> have suggested that migration of certain foreign species can take place primarily through highly mobile intermediate species (e.g., interstitial atoms) that periodically exchange with atoms in the crystalline lattice. Experimental methods for such studies often measure the decay of an artificially created concentration profile. The initial shapes can be delta functions<sup>7</sup> or steps.<sup>6,8,9</sup> The evolution of the profile over time creates various shapes depending on whether the snapshot is taken at short or long times. It has been observed that for sufficiently short times, diffusion profiles decay with “exponential tails,” while for long-time diffusion, the profiles approach Gaussian or error-function forms for initial dopant profiles that are delta or step functions, respectively. In the long-time cases, the profiles can be described via Fick’s law with a single effective diffusivity  $D_{\text{eff}}$ .

At short times, however, a more detailed mechanistic model of the dynamics of intermediate species’ creation, motion, and annihilation is required.<sup>7,10,11</sup> The reaction-diffusion partial differential equations include additional kinetic parameters describing motion and exchange of the intermediate species instead of a single composite diffusion coefficient. Methods have been developed for estimating these kinetic parameters from analytical expressions for the short-time decay of the initial concentration profile.<sup>10,11</sup>

The existing literature suggests that these estimates can be used to calculate  $D_{\text{eff}}$  and therefore the long-term dopant profile. However, various expressions are given for  $D_{\text{eff}}$ , and the applicability of these expressions in various time regimes has remained unclear. This paper derives for a delta function initial profile an exact expression for the effective diffusivity that is valid in all time regimes. It is then shown how the

exact expression can be reduced to literature expressions within certain approximations. Then the approximation error is quantified, and specific recommendations are made to avoid creating mathematical bias in parameter estimates derived from the experimental data.

The governing equations for foreign (dopant) atoms in a solid substrate are<sup>3</sup>

$$\partial C_M / \partial t = D_{\text{hop}} \nabla^2 C_M - K_{\text{ann}} C_M + K_{\text{gen}} C_S, \quad (1)$$

$$\partial (C_S + C_M) / \partial t = D_{\text{hop}} \nabla^2 C_M, \quad (2)$$

where  $D_{\text{hop}}$  denotes the diffusivity of the mobile species, and  $K_{\text{gen}}$  and  $K_{\text{ann}}$  are first-order rate constants for generation and annihilation of mobile species.<sup>12</sup> The subscripts  $M$  and  $S$  refer, respectively, to the mobile species (typically an interstitial foreign atom) and the static species (typically the foreign atom in a substitutional lattice site). Note that Eqs. (1) and (2) show that in the general case, three parameters ( $D_{\text{hop}}$ ,  $K_{\text{gen}}$ , and  $K_{\text{ann}}$ ) are needed to fully characterize the diffusion profile. Yet it is often convenient to model a diffusive process in terms of a single parameter, no matter what the time regime. This description for a fast-mobile-species mechanism would mimic the description for a standard nearest-neighbor jumping mechanism. At long times, dopants that diffuse via mobile species yield profiles that can be accurately described by the single parameter  $D_{\text{eff}}$ . This effective diffusivity itself is a relatively simple composite of other parameters. We seek a more general expression for  $D_{\text{eff}}$  that can accurately describe the diffusional spreading on all time regimes. An analysis in terms of the first and second moments of the profile distribution will provide such an expression.

The moment analysis begins by simply writing a Fick’s law expression for all foreign atoms, either mobile or static. The analysis assumes that  $D_{\text{eff}}$ ,  $K_{\text{gen}}$ , and  $K_{\text{ann}}$  remain invariant with time. Depending on the particular exchange mechanism of the mobile species with the lattice, however,  $K_{\text{gen}}$  and  $K_{\text{ann}}$  can represent composite rate constants that include the concentrations of vacancies or host interstitials. In principle, these concentrations can evolve over time if these spe-

<sup>a)</sup>Electronic mail: braatz@uiuc.edu.

cies exchange with defect clusters, dislocation loops, crystallographic shear planes, or other extended defects whose own concentrations are evolving. However, this evolution is typically slow on the time scale of most diffusion measurements of the type envisioned here. With the constant-parameter assumption, Fick's law becomes

$$\partial(C_S + C_M)/\partial t = D_{\text{eff}}\nabla^2(C_S + C_M). \quad (3)$$

The effective diffusivity  $D_{\text{eff}}$  represents the diffusivity of a single-jump process that will give the same profile as the mobile-species mechanism at long diffusion time.<sup>13</sup> Integrating Eq. (3) over one spatial dimension gives

$$\int_{-\infty}^{\infty} \frac{\partial(C_S + C_M)}{\partial t} dx = \int_{-\infty}^{\infty} D_{\text{eff}} \frac{\partial^2(C_S + C_M)}{\partial x^2} dx, \quad (4)$$

$$\frac{d}{dt}(\mu_{S0} + \mu_{M0}) = D_{\text{eff}} \left. \frac{\partial(C_S + C_M)}{\partial x} \right|_{-\infty}^{\infty} = 0, \quad (5)$$

where  $\mu_{ij} = \int_{-\infty}^{\infty} C_i x^j dx$  is the  $j$ th moment of  $C_i$ . The sum of the zeroth moments of the mobile and static species does not change with time, that is, the total number of atoms in the system is fixed, which is consistent with the assumption that the system is closed. With the assumption that no atoms are initially mobile, temporal integration of Eq. (5) yields

$$\mu_{S0} + \mu_{M0} = \mu_{S0o}. \quad (6)$$

The sum of the second moments is derived from Eq. (3) by multiplying by  $x^2$  and integrating over the spatial coordinate,

$$\int_{-\infty}^{\infty} x^2 \frac{\partial(C_S + C_M)}{\partial t} dx = \int_{-\infty}^{\infty} x^2 D_{\text{eff}} \frac{\partial^2(C_S + C_M)}{\partial x^2} dx, \quad (7)$$

which implies that

$$\begin{aligned} \frac{d}{dt}(\mu_{S2} + \mu_{M2}) &= D_{\text{eff}} x^2 \left. \frac{\partial(C_S + C_M)}{\partial x} \right|_{-\infty}^{\infty} \\ &\quad - D_{\text{eff}} \int_{-\infty}^{\infty} 2x \frac{\partial(C_S + C_M)}{\partial x} dx \\ &= -2D_{\text{eff}} \left[ x(C_S + C_M) \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} (C_S \right. \\ &\quad \left. + C_M) dx \right] \\ &= 2D_{\text{eff}}(\mu_{S0} + \mu_{M0}). \end{aligned} \quad (8a)$$

Temporal integration of this last expression yields

$$\mu_{S2} + \mu_{M2} = 2D_{\text{eff}}\mu_{S0o}t. \quad (8b)$$

Similarly, taking the second moment of Eq. (2) and zeroth moment of Eq. (1) gives

$$\mu_{S2} + \mu_{M2} = 2D_{\text{hop}} \int_0^t \mu_{M0} dt, \quad (9)$$

$$\frac{d}{dt}\mu_{M0} = -K_{\text{ann}}\mu_{M0} + K_{\text{gen}}\mu_{S0}. \quad (10)$$

Integrating Eq. (10) gives

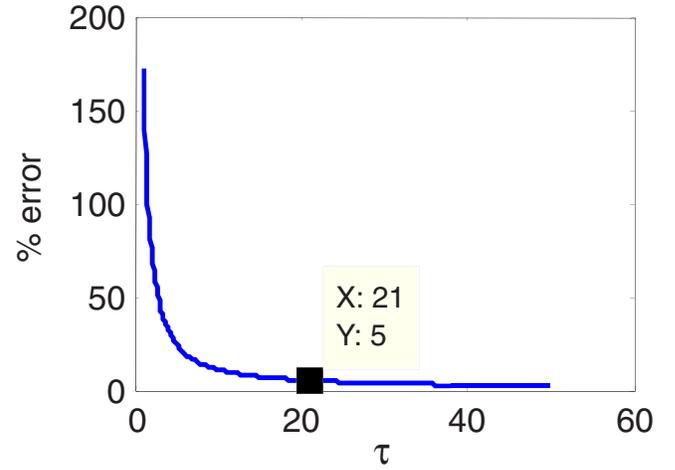


FIG. 1. (Color online) Percent error as a function of dimensionless time  $\tau = (K_{\text{ann}} + K_{\text{gen}})t$ .

$$\mu_{M0} = \frac{K_{\text{gen}}\mu_{S0o}(1 - e^{-(K_{\text{gen}} + K_{\text{ann}})t})}{K_{\text{gen}} + K_{\text{ann}}}. \quad (11)$$

Substituting Eq. (11) into Eq. (9) gives

$$\mu_{S2} + \mu_{M2} = \frac{2D_{\text{hop}}K_{\text{gen}}\mu_{S0o}}{K_{\text{gen}} + K_{\text{ann}}} \left( t - \frac{1 - e^{-(K_{\text{gen}} + K_{\text{ann}})t}}{K_{\text{gen}} + K_{\text{ann}}} \right). \quad (12)$$

Comparing this last expression with Eq. (8b) yields

$$2D_{\text{eff}}\mu_{S0o}t = \frac{2D_{\text{hop}}K_{\text{gen}}\mu_{S0o}}{K_{\text{gen}} + K_{\text{ann}}} \left[ t - \frac{(1 - e^{-(K_{\text{gen}} + K_{\text{ann}})t})}{K_{\text{gen}} + K_{\text{ann}}} \right]. \quad (13a)$$

Simple rearrangement yields the desired general expression for the effective diffusivity,

$$D_{\text{eff}} = \frac{D_{\text{hop}}K_{\text{gen}}}{K_{\text{gen}} + K_{\text{ann}}} \left[ 1 - \frac{(1 - e^{-(K_{\text{gen}} + K_{\text{ann}})t})}{(K_{\text{gen}} + K_{\text{ann}})t} \right]. \quad (13b)$$

The standard deviation of the dopant profiles employs the square root of the ratio of the second and zeroth moments. Thus, in this case the standard deviation is

$$\begin{aligned} \text{sd} &= \sqrt{\frac{\mu_{S2} + \mu_{M2}}{\mu_{S0} + \mu_{M0}}} = \sqrt{2D_{\text{eff}}t} \\ &= \sqrt{2 \frac{D_{\text{hop}}K_{\text{gen}}}{K_{\text{gen}} + K_{\text{ann}}} \left( t - \frac{1 - e^{-(K_{\text{gen}} + K_{\text{ann}})t}}{K_{\text{gen}} + K_{\text{ann}}} \right)}. \end{aligned} \quad (13c)$$

This expression based on a nearest-neighbor-hopping mechanism exactly matches the standard deviation of the dopant concentration profile given by the governing equations for mobile-intermediate diffusion [Eqs. (1) and (2)]. That is, the effective diffusivity in Eq. (13b) is the value that exactly captures the amount of spreading of the dopant profile in any time regime. As is standard in diffusion problems,<sup>14</sup> this spreading has been quantified in terms of the squared distance from the position of the initial dopant.

For large  $t$ , expressions (13b) and (13c) asymptotically approach

$$D_{\text{eff}} = \frac{D_{\text{hop}}K_{\text{gen}}}{K_{\text{gen}} + K_{\text{ann}}}, \quad (14a)$$

$$sd = \sqrt{2 \frac{D_{\text{hop}} K_{\text{gen}} t}{K_{\text{gen}} + K_{\text{ann}}}}. \quad (14b)$$

In literature, the long-time effective diffusivity has been given as<sup>15</sup>

$$D_{\text{eff}} = \frac{D_{\text{hop}} K_{\text{gen}}}{K_{\text{ann}}}, \quad (15a)$$

$$sd = \sqrt{2 \frac{D_{\text{hop}} K_{\text{gen}} t}{K_{\text{ann}}}}. \quad (15b)$$

These expressions are not quite as accurate as Eqs. (14a) and (14b) but are sufficient provided that  $K_{\text{gen}} \ll K_{\text{ann}}$ . By hypoth-

esis, mobile foreign atoms exist in much smaller concentrations than static substitutional atoms and can be considered as unstable intermediates in a chemical reaction. The classical quasi-steady-state approximation can then be applied to mobile species, implying that  $\partial C_M / \partial t \approx 0$ . This condition is equivalent to  $K_{\text{gen}} \ll K_{\text{ann}}$ . At this limit, Eq. (15a) for the effective diffusivity has also been formulated as<sup>7,10,11</sup>

$$D_{\text{eff}} = K_{\text{gen}} \lambda^2, \quad (16)$$

where  $\lambda = \sqrt{D_{\text{hop}} / K_{\text{ann}}}$  represents a mean path length between generation and annihilation events.

The error in approximating Eq. (13b) with Eq. (14a) is<sup>16</sup>

$$\% \text{ error} = \frac{\frac{D_{\text{hop}} K_{\text{gen}}}{K_{\text{gen}} + K_{\text{ann}}} - \frac{D_{\text{hop}} K_{\text{gen}}}{K_{\text{gen}} + K_{\text{ann}}} \left[ 1 - \frac{(1 - e^{-(K_{\text{gen}} + K_{\text{ann}})t})}{(K_{\text{gen}} + K_{\text{ann}})t} \right]}{\frac{D_{\text{hop}} K_{\text{gen}}}{K_{\text{gen}} + K_{\text{ann}}} \left[ 1 - \frac{(1 - e^{-(K_{\text{gen}} + K_{\text{ann}})t})}{(K_{\text{gen}} + K_{\text{ann}})t} \right]} (100) = \frac{1 - e^{-\tau}}{\tau - (1 - e^{-\tau})} (100), \quad (17)$$

which is a function of only one dimensionless group  $\tau = (K_{\text{ann}} + K_{\text{gen}})t$ . The error decays rather slowly with respect to time as  $1/t$ . Equation (17) can be used to estimate how much time should pass before Eq. (14) can be applied to avoid biasing the parameter estimates. It can be seen from Fig. 1 that the error decreases to less than 5% only for  $\tau > 21$ .

The quantitative relative error in approximating Eq. (14a) with Eq. (15a) is

$$\frac{\frac{D_{\text{hop}} K_{\text{gen}}}{K_{\text{ann}}} - \frac{D_{\text{hop}} K_{\text{gen}}}{K_{\text{gen}} + K_{\text{ann}}}}{\frac{D_{\text{hop}} K_{\text{gen}}}{K_{\text{gen}} + K_{\text{ann}}}} = \frac{K_{\text{gen}}}{K_{\text{ann}}}. \quad (18)$$

Equation (18) indicates that the error in this second approximation is  $< 1\%$  provided that the kinetic constant for the generation of mobile species is  $< 1\%$  of the kinetic constant for the annihilation of mobile species.

A general expression is derived for estimating the effective diffusivity in point defect-mediated diffusion with a fast-mobile-species mechanism. The key time scale for characterizing the dynamic approach of the reaction-diffusion process to behave like a single-jump diffusion process is  $1/(K_{\text{ann}} + K_{\text{gen}})$ , and it is shown that  $\sim 20/(K_{\text{ann}} + K_{\text{gen}})$  is required to produce an error of  $\sim 5\%$  or less in the spreading of the total dopant concentration profile.

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<sup>12</sup> $K_{\text{gen}}$  and  $K_{\text{ann}}$  correspond to  $g$  and  $r$  used by Cowern *et al.* (Ref. 10) and  $D_{\text{hop}}$  corresponds to  $D_m$  used by Cowern *et al.* (Ref. 10) and  $D_M$  used by Vaidyanathan *et al.* (Ref. 11).

<sup>13</sup> $D_{\text{eff}}$  is referred to as an "average diffusivity  $D$ " by Cowern *et al.* (Ref. 10) and "effective diffusivity" by Vaidyanathan *et al.* (Ref. 11).

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<sup>15</sup>After accounting for notational differences, these expressions can be found halfway down column 2 on p. 2436 of Ref. 7, top of column 2 on p. 212 and Eq. (6) of Ref. 10, and top of column 2 on p. 367 and Eq. (13) of Ref. 11.

<sup>16</sup>Similar analysis can be applied to analyze approximation errors for the standard deviation.