Atomistic Models of Vacancy-Mediated Dopant Diffusion in Silicon at High Doping Levels

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Abstract

This paper uses Monte-Carlo simulation on the silicon lattice to investigate vacancy-mediated dopant diffusion. By considering vacancy/dopant interaction potentials which extend out to third-nearest-neighbor distances as required for pair diffusion theories, we observe the very rapid increase in dopant diffusivity at concentrations above $2 \times 10^{20} \text{cm}^{-3}$ that has been observed experimentally for group IV and V atoms in silicon [1]. We also derive an improved analytic expression for dopant diffusivity at low and moderate doping levels as a function of interaction potential that agrees with the simulation results. Further simulations verify the the central role of third-nearest-neighbor interactions to vacancy-mediated diffusion in silicon.

1 Introduction

The diffusion of dopant atoms in silicon takes place via interactions with point defects, interstitials and vacancies [2]. Understanding the details of defect-mediated diffusion is essential in order to correctly model dopant diffusion in silicon. In addition, the analysis provides the connection between the atomistic interactions, for which parameters may be calculated based on *ab initio* theory, and macroscopic phenomenological models used in process simulators based on continuity equations. In this work, we analyze the interactions of dopants with vacancies and find that the assumptions inherent in pair diffusion models lead to greatly enhanced dopant diffusion at high doping concentrations. This phenomena has been observed experimentally for vacancy diffusers in silicon (Sb, As, Ge, Sn) [1], but is not typically included in process simulation. In our analysis, we develop approximate analytic models and confirm the results using full three-dimensional Monte-Carlo simulations on the silicon (diamond) lattice.

2 Modeling of Vacancy-Mediated Diffusion

The observation that dopant diffusivity is much more rapid than silicon self-diffusion leads to the conclusion that there exists an attractive potential between dopants and defects that results in the formation of dopant/defect pairs. However, due to the silicon lattice structure, the vacancy must move away to at least a third-nearest-neighbor site in order to return along a different path. Thus, the pair must partially dissociate and reform many times before finally fully dissociating, with the third-nearest-neighbor sites playing a critical role.

Diffusivity due to hopping diffusion can written as $D = \alpha^2 \nu_{\text{eff}}$, where $\alpha = a/4$ is the jump distance in the principal direction of diffusion and ν_{eff} the effective mean hopping rate if each dopant hop was uncorrelated to previous hops. For vacancy-mediated dopant diffusion, the effective hopping rate is much smaller than the actual rate of dopant displacement since dopants can be expected to exchange places many times with a nearest-neighbor vacancy without resulting in any net dopant motion (equivalent to a correlation factor much less than one). Focusing on the pivotal role of the third-nearest neighbor sites, we find that the effective hopping rate can be written as $\nu_{\text{eff}} = p_B \left[C_{DV}^3 / C_D\right] (\nu_{32})$, where $p_B = 1/3$ is the effective fraction of third-nearest neighbor sites acting to bridge subsequent jumps in the opposite direction, C_{DV}^3 is the number of third-nearest-neighbor dopant/vacancy pairs, C_D is the doping density, and ν_{32} is the hopping rate of vacancies from third to second-nearest neighbor sites. Substituting in the appropriate expressions,

$$D = \frac{\alpha^2}{3}\left[12\left(\frac{C_V^\infty}{C_s}\right)\exp\left(\frac{\Delta E_3}{kT}\right)\right]\left[\nu_0 \exp\left(\frac{\Delta E_2 - \Delta E_3}{2kT}\right)\right] = 4\alpha^2\left(\frac{C_V^\infty}{C_s}\right)\nu_0 \exp\left(\frac{\Delta E_2 + \Delta E_3}{2kT}\right) \tag{1}$$

where C_V^∞ is the equilibrium vacancy concentration far from a dopant atom, ν_0 is the vacancy hopping rate in undoped material, ΔE_i is dopant/vacancy binding energy for the i^{th}-nearest-neighbor sites, and it was assumed that the presence of dopants causes a linear variation in energy (and thus diffusion barrier) between lattice sites. Note that this expression differs from the work of Hu [3] in explicitly specifying the pre-exponential term and replacing ΔE_3 with $(\Delta E_2 + \Delta E_3)/2$, resulting in an improved match to Hu's numerical results.

If the dopant density is very low, it is reasonable to assume that each vacancy interacts with at most one dopant atom, and ΔE_2 and ΔE_3 are simply as given for interactions with a single dopant. However, in heavily-doped material, a vacancy is likely to interact with more than one dopant at a time, increasing the probability of finding a vacancy at a third-nearest-neighbor site and thereby increasing the dopant diffusivity. To estimate the effect of such interactions, ν_{eff} becomes a weighted average of rates over all possible dopant configurations in the neighborhood of a vacancy, resulting in

$$D = D^{\text{int}}\left[1 + \beta_1\left(\frac{C_D}{C_s - C_D}\right) + \beta_2\left(\frac{C_D}{C_s - C_D}\right)^2 + \ldots\right], \tag{2}$$

where the β_i can be calculated from averages over interactions of vacancies with $i+1$ dopant atoms.

3 Lattice Monte-Carlo Simulations

In order to test the analytic model, as well as to consider more complicated interactions, we conducted a series of atomistic Monte-Carlo simulations of vacancy movement on a doped silicon lattice. To account for the interaction potential between the vacancy and dopant, the vacancy hopping probabilities were biased based on the distribution of dopants in their neighborhood, with the potential assumed to depend on the number of dopants on neighboring sites according to

$$\Delta E = -(n_1 \Delta E_1 + n_2 \Delta E_2 + n_3 \Delta E_3), \tag{3}$$

where n_i represents the number of dopant atoms on i^{th}-nearest-neighbor sites. The simulations were conducted on an $N_x \times N_y \times N_z$ array of cubic cells, each with 8 lattice sites, with the $4 \times N_V$ hopping probabilities calculated based on the dopant distribution in the neighborhoods of the vacancies before and after hopping. Vacancy hops are considered in a serial fashion, based on the relative hopping rates, with hopping rates recalculated only when they are altered. At each step, the expected time before the first vacancy hops is given by

$$\Delta t = \left[\sum_{i=1}^{N_V} \sum_{j=1}^{4} \nu_i^j \right]^{-1}, \tag{4}$$

so the time is incremented by this amount following each hop. In order to determine the dopant diffusivity, the average displacement of dopant atoms over the course of the simulation was calculated to give $D = \langle \Delta \vec{x}^2 \rangle / 2t$.

According to our analysis (Eq. (1)), dopant diffusivity via dopant/vacancies pairs can be expected to depend critically on the number of third-nearest-neighbor pairs and the activation barrier for hopping to the second-nearest-neighbor sites, but is independent of the the nearest-neighbor binding energy, which dominates the number of dopant/vacancy pairs. To check this theory, we conducted a series of simulations in which the the pair binding energy (ΔE_1) and the third-nearest-neighbor binding energy (ΔE_3) were varied. The simulation results confirm that the diffusivity is almost independent of the nearest-neighbor binding energy, providing that there exists vacancy source/sinks to maintain the vacancy concentration near equilibrium. In contrast, dopant diffusivity has a strong dependence on the third-nearest neighbor binding energy as predicted, confirming that such long-range interactions are required in order for the dopant diffusivity for vacancy diffusers to be orders of magnitude above silicon self-diffusion as observed experimentally [2].

As described above, at very high concentrations, we expect dopant diffusivity to increase sharply with doping density as the interactions of vacancies with multiple dopants reduces the migration energy of the dopant/vacancy pair. Simulation results confirming this concept are shown in Figure 1. The behavior observed here is consistent with the observations of Larsen *et al.* [1] of enhanced dopant diffusivity at concentrations above $2 \times 10^{20}\mathrm{cm}^{-3}$. However, the enhanced diffusion does not exhibit the abrupt increase typical of percolation as suggested by Mathiot and Pfister [4], but rather has a more gradual onset, which is more consistent with the experimental observations as well as the polynomial behavior expected based on our analysis. The diffusivity values are normalized by the density of isolated vacancies, which eliminates the effect of Fermi level changes with increased doping. At very high concentrations, the normalized diffusivity varies as C_D^n with $n \cong 3$. For diffusion with singly-charged vacancies, adding in the Fermi level dependence gives $n = 4$, which is very similar to the values measured by Larsen *et al.* [1], which vary from 3.5 to 5. Note that for the simulation results shown in Figure 1, the rapid increase in diffusivity occurs at about $5 \times 10^{20}\mathrm{cm}^{-3}$, higher than measured experimentally. This is likely due to the truncation of the interaction potential at the third-nearest-neighbor distance.

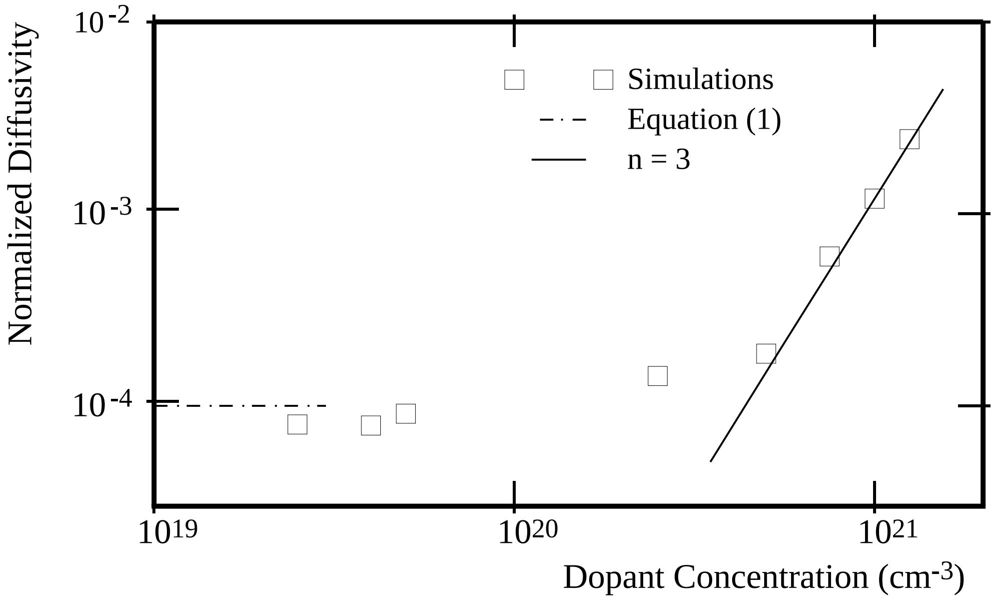

Figure 1: *Normalized dopant diffusivity* $D/(a^2\nu_0 C_{\mathrm{V}}^{\infty})$ *versus doping density calculated from lattice Monte-Carlo simulations. Included for comparison is the estimated diffusivity at low doping levels as given by Equation (1) and* KC_D^n *with* $n = 3$*.*

4 Conclusions

In summary, we have developed an atomistic theory for dopant diffusion via vacancy interactions and validated the predictions of that theory using lattice Monte-Carlo simulations. The analysis provides a correction to previous work of Hu [3] at low doping levels and confirms the central role of third-nearest-neighbor interactions. Both analysis and simulation show that full consideration of the assumptions inherent in pair diffusion models requires that the effective pair diffusivity will increase at high doping concentrations, with an approximately polynomial dependence on the doping density. The simulations show a dependence of diffusivity on doping level that is consistent with experimental measurements for vacancy diffusers in silicon (Sb, As, Ge and Sn).

This work was supported by NSF Contract #ECS-9009591 and SRC/SEMATECH Contracts #91-MC-503 and #93-MJ-530.

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