Lattice Monte-Carlo Simulations of Vacancy-Mediated Diffusion and Implications for Continuum Models of Coupled Diffusion

S. T. Dunham and C. D. Wu

Department of Electrical, Computer and Systems Engineering
Boston University, Boston, MA 02215, USA

Abstract

In this paper, we analyze the interactions of dopants with vacancies using Lattice Monte-Carlo simulations and find that the assumptions underlying pair diffusion models lead to several corrections to the standard continuum models for coupled dopant/defect diffusion. Specifically, we find that at high doping levels, both the effective pair diffusivity as well self-diffusion due to vacancies increase rapidly with doping level due to the interactions of vacancies with multiple dopants. In addition, we find that pair diffusion theories overestimate the dopant flux resulting from gradients in the vacancy concentration.

Pair diffusion models have been very effective in modeling the coupled diffusion of dopants and point defects in silicon [1, 2, 3, 4]. However, the structure of the silicon lattice and the fact that the vacancy and the dopant move in opposite directions during exchanges, leads to a violation of the basic underlying assumption – that a dopant and a vacancy move together as a tightly-coupled pair. Lattice Monte-Carlo (LMC) simulations as used in this work provide a powerful tool for investigating vacancy-mediated dopant diffusion and provide information on how to modify pair diffusion models to better account for the underlying atomistic behavior.

The LMC simulations involve the hopping of vacancy atoms on a doped silicon lattice, with site exchanges with dopant atoms resulting in dopant diffusion. The vacancy hopping probabilities are biased by the dopant/vacancy interaction potential leading to the formation and diffusion of dopant/vacancy pairs. Since diffusion of a dopant/vacancy pair on the diamond lattice requires the vacancy to move away to at least a third-nearest-neighbor (3NN) distance, we consider a dopant/vacancy interaction out to 3NN sites. For the first-nearest neighbor binding energies, we used the experimental lower bounds for arsenic (1.23 eV) or phosphorus (1.04 eV) from Hirata *et al.* [5]. Since data is unavailable for the second and third-nearest neighbor binding energies, we simply used 2/3 and 1/3 of the nearest neighbor energy, respectively.

At very high doping levels, a vacancy is likely to interact with more than one dopant at a time. The net result is to reduce the activation energy for pair diffusion associated with third to second-nearest neighbor transitions, thereby increasing the dopant diffusivity. This behavior has been observed experimentally for group IV and V dopants in phosphorus-doped silicon by Nylandsted Larsen *et al.* [6]. Figure 1 illustrates how

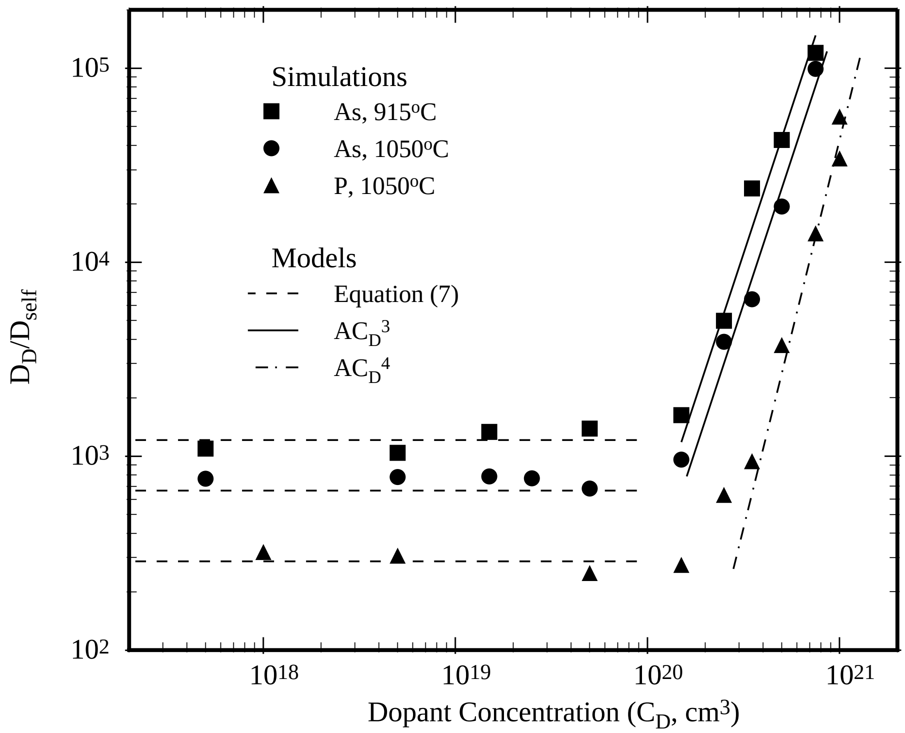

Figure 1: *Normalized diffusivity versus doping density using the pair binding energy for arsenic and phosphorus [5]. At high concentrations, the normalized diffusivity is approximately proportional to C_D^n with $3 < n < 4$ as indicated. Also shown for comparison is the analytic predictions for diffusivity in moderately doped material [7].*

dopant diffusivity as obtained from the LMC simulations varies as a function of doping level. The normalized diffusivity is nearly uniform at low and moderate doping levels and then rises rapidly for doping levels above about $2 \times 10^{20}\mathrm{cm}^{-3}$, manifesting an approximate third or fourth power dependence on the doping level. The results of the simulations agree well with the experimental observations of Nylandsted Larsen *et al.* [6], with a good match to both the doping level at which the onset of enhanced pair diffusion is observed and the dependence of diffusivity with increasing concentration (4th or 5th power dependence on doping once Fermi level effects are included).

The interaction of vacancies with multiple dopants can also be expected to increase self-diffusion via vacancies ($D_V C_V^*$) beyond just Fermi level effects, since vacancies can potentially travel long distances by transferring from one dopant to another. We examined vacancy density and displacement during LMC simulations and found that indeed the increase in self-diffusion via vacancies with doping level substantially exceeds that due simply to pair diffusion. Fig. 2 plots the components of self-diffusion via vacancies versus doping level as derived from the simulation results. The LMC simulations do not distinguish between paired and unpaired vacancies (indeed, vacancies switch during the course of the simulation), so within the pair diffusion formalism, we can break up the vacancy displacement into two parts, one part which is associated with the motion of dopant/vacancy pairs, and a second part which is due to the increase in loosely-bound vacancies which can move from the neighborhood of one dopant to another (equivalent to reduction in the quasi-vacancy formation energy [1]). The initial increase in vacancy displacement is primarily due to the displacement of loosely-bound vacancies, with the diffusion of pairs dominating at very high doping levels.

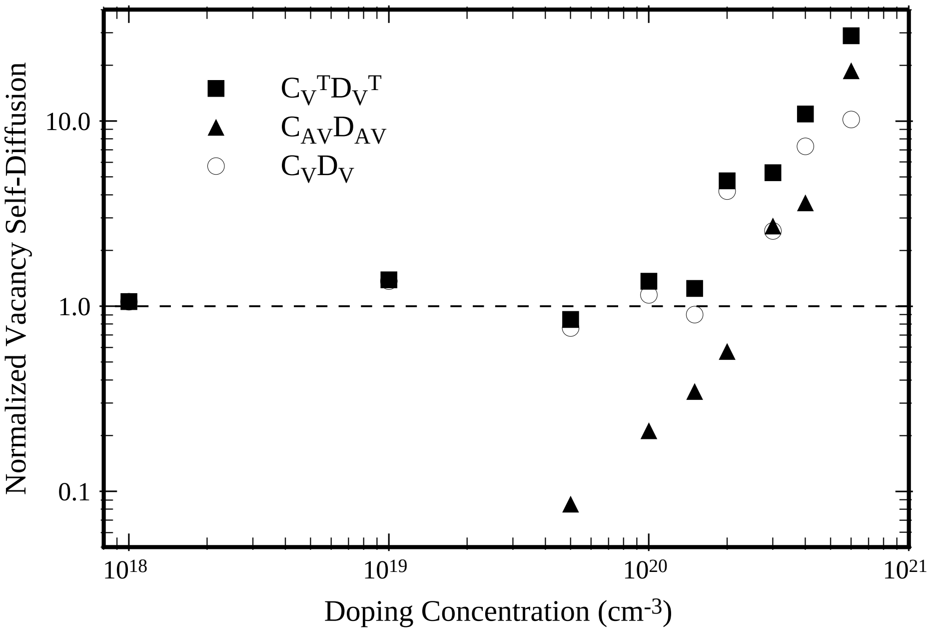

Figure 2: *Vacancy self-diffusion normalized by its value in intrinsic material, with Fermi-level effects ignored, as a function of doping concentration for arsenic at 1050°C (or phosphorus at 850°C). Plotted are the total vacancy displacement, the vacancy displacement due to pair diffusion and the vacancy displacement due to diffusion of unpaired vacancies, which is calculated from the difference of the first two quantities.*

The formation of a high-concentration plateau in phosphorus diffusion profiles has been previously been accounted for by both enhanced pair diffusion [2, 3, 8, 9] and enhanced self-diffusion via vacancies [1]. This work shows that both effects can in fact be expected to operate in such systems. The combination of the two effects leads to a more pronounced plateau and sharper kink than with either of the effects acting alone.

In addition to examining diffusion in homogeneous systems, we also investigated the effect of a vacancy gradient on the motion of dopants via LMC. Pair diffusion models predict that the flux of dopants due diffusion via vacancies is given by:

$$J_A^V = -D_{AV} K_{A/V} \left(C_V \bigtriangledown C_A + C_A \bigtriangledown C_V \right), \tag{1}$$

while simple vacancy diffusion theories [10] imply that the the sign of the second term is reversed since a dopant/vacancy exchange results in the dopant and vacancy moving in opposite directions. A vacancy gradient was sustained by adding an energy discontinuity along the $z = 0$ plane. The LMC simulations show that

$$J_A^V = -D_{AV} K_{A/V} \left(C_V \bigtriangledown C_A + \gamma C_A \bigtriangledown C_V \right), \tag{2}$$

where γ is a function of the dopant/vacancy interaction potential. For the binding energies used in this work, we find $\gamma \cong 1/3$ as illustrated in Fig. 3, consistent with the value of 0.55 calculated by List *et al.* [11] for a stronger 3NN interaction.

In summary, Lattice Monte-Carlo simulations show that the coupled diffusion of vacancies and dopants deviates from ideal pair-diffusion behavior. At high doping levels, the interactions of vacancies with multiple dopants leads to rapid increases of both dopant diffusion and self-diffusion via vacancies at high doping levels. These effects

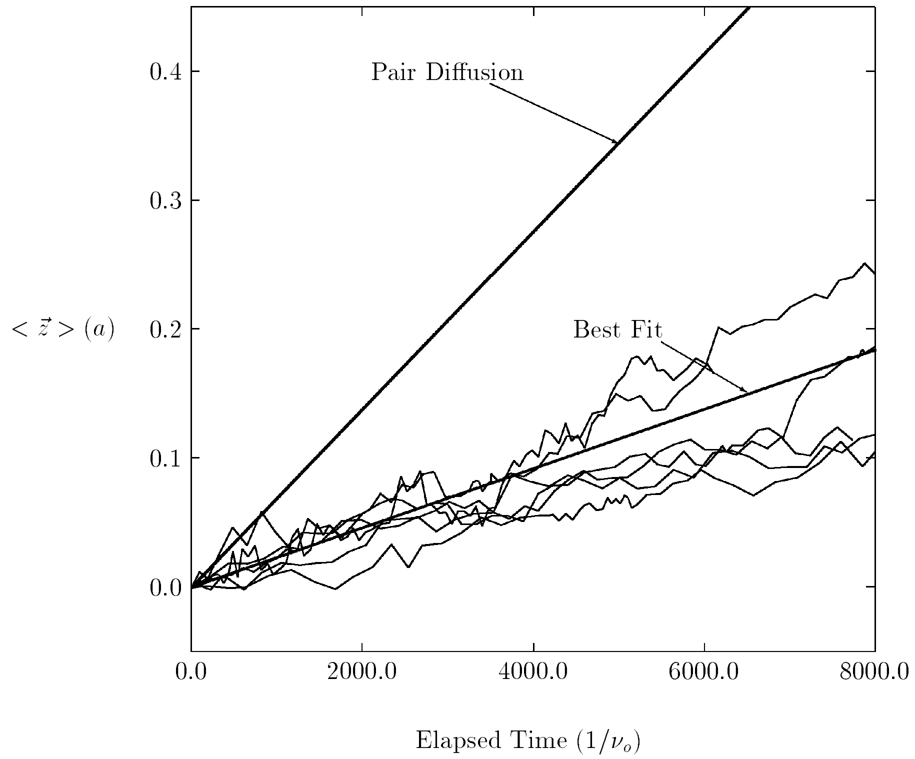

Figure 3: *Average dopant displacement versus time in the presence of a vacancy gradient.*

lead to the plateau observed in the high concentration region of phosphorus diffusion profiles. At moderate doping levels, the fact that vacancies and dopants cannot diffuse together as a tightly coupled pair leads to a reduction in the flux of dopants in a vacancy gradient relative to that predicted by pair-diffusion theories.

This work was supported by SRC/SEMATECH and NSF.

References

[1] M. Yoshida, *Jap. J. Appl. Phys.* **22**, 1404 (1983).

[2] D. Mathiot and J. C. Pfister, *J. Appl. Phys.* **55**, 3518 (1984).

[3] S. T. Dunham, *J. Electrochem. Soc.* **139**, 2628 (1992).

[4] P. M. Fahey, P. B. Griffin and J. D. Plummer, *Rev. Mod. Phys.* **61**, 289 (1989).

[5] M. Hirata, M. Hirata and H. Saito, *J. Phys. Soc. Jap.* **27**, 405 (1969).

[6] A. Nylandsted Larsen, K. Kyllesbech Larsen, P. E. Andersen, B. G. Svensson, *J. Appl. Phys.* **73**, 691 (1993).

[7] S. T. Dunham and C. D. Wu, **NUPAD V Proceedings**, 101 (1994).

[8] D. Mathiot and J. C. Pfister, *J. Phys. Lett.* **43**, L-453 (1982).

[9] D. Mathiot and J. C. Pfister, *J. Appl. Phys.* **66**, 1970 (1989).

[10] K. Maser, *Expt. Tech. Phys.* **39**, 169 (1991).

[11] S. List, P. Pichler and H. Ryssel, *J. Appl. Phys.* **76**, 223 (1994).