To appear in *J. Appl. Phys.* **79(9)** (1996).

Reply to "A Comment on 'Atomistic Models of Vacancy-Mediated Diffusion in Silicon' "

[*J. Appl. Phys.* **78**, 2362 (1995)]

Scott T. Dunham

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

Abstract

Antoncik has criticized both the conclusions and elements of the modeling approach in a previously published paper on dopant diffusion in silicon [*J. Appl. Phys.* **78**, 2362 (1995)]. As is shown in this reply, those criticisms are without merit and the alternative explanation proposed to explain the rapid diffusivity increase observed at high donor concentrations is based on an analysis which contains a series of critical errors, most prominently the association of the solubility limit with the number of possible donor sites within the crystal.

The preceding "Comment" by Antoncik [1] includes two main criticisms of our work [2]: that the conclusions are "questionable" because dopant/dopant interaction arising from a limited number of available sites are not accounted for, and that we used an "assumed" or "*ad hoc*" form for the diffusion coefficient dependence on doping concentration. Both criticisms are unwarranted and appear to indicate a lack of understanding of our work, as well as solid state diffusion and aggregation processes in general. We begin our response by directly rebutting these criticisms and continue by pointing out the fundamental errors underlying the alternative analysis proposed by Antoncik [1,3-9].

Antoncik's [1] first point is that our "conclusion that the very high increase of D_{eff} at high concentrations is 'due to interactions of vacancies with more than one dopant atom' " [2] is "questionable" because it "did not take into account the interaction of the dopant atom with its neighboring dopant atoms." To begin, it should be noted that the conclusion quoted above actually refers to the *simulations*, not the experiments [2]. Since no direct dopant/dopant interactions are present in our simulations, they are clearly *not* the source of the resulting behavior. In fact, what is most notable about the results of the atomistic simulations is that simply by implementing a dopant/vacancy attraction out to third-nearest-neighbor distances, as required for dopant/vacancy pair diffusion models, we are led directly to a rapid increase in diffusivity at high doping levels that matches both the point of onset and doping dependence of the experimentally-observed diffusivity enhancement [2]. It is certainly possible that other phenomena may also be important in the physical system; however, the close agreement between simulations and experiments is highly suggestive that the phenomena considered in Ref. 2 is in fact the primary cause of the experimental behavior. In his criticism, Antoncik provides an alternative model to account for the experimental behavior observed by Nylandsted Larsen *et al.* [10] to which we compare our simulation results. This model, which has been previously discussed at great length in a series of papers [3-9], does not provide a plausible alternative explanation since, as will be shown below, it is based on faulty assumptions regarding the basic processes which limit equilibrium solid solubility and control pair formation/dissolution. There certainly are direct dopant/dopant interactions which lead to dopant aggregation and deactivation in silicon, but not of the type assumed in the Antoncik model.

The second, more general criticism is that the dependence of the diffusivity on doping concentration derived in Ref. 2 is based on "ad hoc assumptions" [1] rather than on the underlying physical processes, suggesting that the form of the solution was chosen to match the experiment in question. This criticism is particularly ironic given the the fact that the lattice Monte Carlo method [2] directly models the fundamental discrete hopping processes of the physical system, which can only be approximated by continuum reaction-diffusion equations such as that suggested by Antoncik. Moreover, these simulations are able to predict how donor diffusivity increases at high doping levels without requiring *any* empirical fitting parameters. In order to simplify the application of the simulation results, we do use a polynomial expansion, but this expression has a direct physical basis as described in the text supporting Eq. (8) in Ref. 2. Contrary to claims by Antoncik [3-7], the use of Fermi level dependent diffusivities as in Eq. (14) in Ref. 2 is based on a rigorous analysis [11] and successfully accounts for a large range of experimental data (see Ref. 11 and references therein). In contrast, the model proposed in Ref. 1 does *not* match experimental results. For example, the model does not manifest the linear dependence of dopant diffusivity on doping seen at moderate doping levels [12-15].[1] Antoncik [7] points out that Eq. (1) in Ref. 1 reduces to a linear dependence for small values of u_{d}, but fails to realize that under these conditions, the linear term is much smaller than the constant term. Thus, as is evident from Fig. 1 in Ref. 1, the model never displays the dominantly linear behavior observed experimentally [12-15]. In fact, despite extensive claims regarding the ability of the Antoncik model to match experiments, direct comparisons of that model to experimental results are notably lacking [1,3-9].

Since it provides the basis for the arguments in Ref. 1, we return to the model proposed by Antoncik and show that it is based on a series of faulty assumptions. The reaction/diffusion equations proposed by Antoncik for the concentrations of donors u_{d} and donor/vacancy pairs u_{p} are:

$$\frac{du_{\mathrm{d}}}{dt} = k_d\theta\,(u_{\mathrm{d\,max}} - u_{\mathrm{d}})\,(1 - u_{\mathrm{d}}/u_{\mathrm{d\,max}})\,u_{\mathrm{p}} - k_{\mathrm{p}}u_{\mathrm{v}}u_{\mathrm{d}} \tag{1}$$

$$\frac{du_{\mathrm{p}}}{dt} = D_{\mathrm{p}}\frac{\partial^2 u_{\mathrm{p}}}{\partial^2 x} - k_d\theta\,(u_{\mathrm{d\,max}} - u_{\mathrm{d}})\,(1 - u_{\mathrm{d}}/u_{\mathrm{d\,max}})\,u_{\mathrm{p}} + k_{\mathrm{p}}u_{\mathrm{v}}u_{\mathrm{d}}, \tag{2}$$

where k_{p} and k_{d} are the rates of the donor/vacancy pair formation and dissolution reactions, $\theta(x) = 1$ for $x \geq 0$ and $\theta(x) = 0$ for $x < 0$, D_{p} is the pair diffusivity, u_{v} is the vacancy concentration and $u_{\mathrm{d\,max}}$ is the "local solubility limit" [3,6-9]. Given these equations and the assumptions that the pairing process is rapid relative to the evolution of the concentrations and that only paired donors diffuse, the effective diffusivity of the total donor concentration (paired and unpaired) can be written as [1,7-9]:

$$D_{\mathrm{eff}} = \frac{D_p}{1 + K(1 - u_{\mathrm{d}}/u_{\mathrm{d\,max}})^2}, \tag{3}$$

where $K = (k_d u_{\mathrm{d\,max}})/(k_p u_v) \gg 1$ (not $K = k_d/(k_p u_v)$ as given in Refs. 7, 8 and 9).

[1] Clearly such behavior can be included by using a linear dependence of vacancy concentration on doping (as in Refs. 3 and 4), but this is the same Fermi level dependent model that Antoncik denounces [3-7].

Equations (1) and (2) along with the continuity equation for vacancies would represent a simplified set of standard coupled equations for vacancy-mediated diffusion [16] if standard pair dissolution rate terms ($k_\mathrm{d} u_\mathrm{p}$) were used. Instead three extra factors are added. Since the system being considered is for $x \geq 0$, the first factor, θ can be safely be ignored. The second factor ($u_{\mathrm{d\,max}} - u_\mathrm{d}$) is attributed to the "number of accessible sites" [9]. Finally, the third factor ($1 - u_\mathrm{d}/u_{\mathrm{d\,max}}$) is identified as "a simple probability factor..., taking into account the limited number of available donor sites" [3]. Within the Antoncik model, the huge increase of D_eff in Eq. (3) as u_d approaches $u_{\mathrm{d\,max}}$ (as illustrated in Fig. 1 of Ref. 1) can be directly attributed to an increased ratio of pairs (mobile) to donors (immobile), which is due to these extra factors in the pair dissolution rate and the corresponding absence of such terms in the pairing rate.

One problem to be noted is that the last two extra factors both account for the same phenomena, the limited number of available sites, thus double-counting the effect.[2] The larger problem, as we discuss further below, is that there is no basis for suggesting that $u_{\mathrm{d\,max}}$ is on the order of the solubility, since for a substitutional donor the number of sites is by definition the number of silicon lattice sites, more than two orders of magnitude larger. Finally, even if one accepts the tenet that there is a smaller limit to the number of donor sites, the pair dissolution rate would be unaffected since a donor/vacancy pair already occupies *two* lattice sites. Pair dissolution simply requires that the vacancy move away.

As is well established [11], equilibrium solid solubility limits for dopants in silicon are due to the formation of dopant-rich clusters or precipitates. In contrast to assertions made by Antoncik [1,3-9] based on an inappropriate analogy to the Langmuir isotherm, solubility is not due to any limit on the number of substitutional donor sites, but rather the fact that dopant aggregation becomes energetically favorable at high doping levels (see for example [17] and references therein). In fact, there is direct experimental evidence to the contrary in that laser annealed or molecular beam epitaxy grown samples can show active donor concentrations more than an order of magnitude above the equilibrium solubility level [18-20].

The work of Bakeman and Borrego [21] is cited to support the approach used by Antoncik [1, 7]. As in Refs 1, 3-9, the analysis in Ref. 21 is based on the fallacy that the solubility limit in silicon is due to a limited number of dopant sites. Within the framework of simple hopping diffusion (no point defects or pairs), Bakeman and Borrego make a further error by assuming that the total impurity jump frequency Γ is independent of the number of available sites. Thus, while in lightly doped material the hopping rate into each of 4 adjacent sites is $\Gamma/4$, as the occupation probability approaches 1 the hopping rate to remaining open sites becomes infinite, leading to a corresponding rapid increase in diffusivity. The correct analysis would keep the hopping rate to an open site fixed and leads to a diffusivity which is independent of concentration.

In summary, the arguments made in Ref. 1 criticizing the conclusions and general approach of Ref. 2 are without merit and the alternative explanation proposed is based on an analysis which contains a series of critical errors, most prominently the association of the solubility limit with the number of possible donor sites within the crystal.

[2] By dropping the square in Eq. (3) as was done in earlier papers by Antoncik [3, 4], the double counting is cancelled, giving the expected behavior for the proposed system.

References

[1] E. Antoncik, *J. Appl. Phys.* (1996).

[2] S. T. Dunham and C. D. Wu, *J. Appl. Phys.* **78**, 2362 (1995).

[3] E. Antoncik, *Appl. Phys. A* **56**, 291 (1993).

[4] E. Antoncik, *Nucl. Instrum. Methods B* **80/81**, 998 (1993).

[5] E. Antoncik, *Appl. Phys. Lett.* **65**, 1320 (1994).

[6] E. Antoncik, *Appl. Phys. A* **58**, 117 (1994).

[7] E. Antoncik, *J. Electrochem. Soc.* **141**, 3593 (1994).

[8] E. Antoncik, *J. Electrochem. Soc.* **142**, 3170 (1995).

[9] E. Antoncik, *Phys. Stat. Sol. A* **149**, 557 (1995).

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

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

[12] J. Makris and B. Masters, J. Electrochem. Soc. **120**, 1252 (1973).

[13] F. Wittel and S. T. Dunham, *Appl. Phys. Lett.* **66**, 1415 (1995).

[14] R. Fair, *Impurity Doping in Silicon*, edited by F. Wang, (North-Holland, New York, 1981), pp. 315-442.

[15] R. Fair, M. Manda, and J. Wortman, J. Mater. Res. **1**, 705 (1986).

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

[17] J. W. Christian in **The Theory of Transformations in Metals and Alloys, Part I, 2nd ed.**, (New York, Pergamon Press, 1981).

[18] D. Nobili, A. Carabelas, G. Celotti and S. Solmi, *J. Electrochem. Soc.* **130**, 922 (1983).

[19] M. Finetti, P. Negrini, S. Solmi and D. Nobili, *J. Electrochem. Soc.* **128**, 1313 (1981).

[20] H.-J. Gossmann, F. C. Unterwald and H. S. Luftman, *J. Appl. Phys.* **73**, 8237 (1993).

[21] P. E. Bakeman, Jr. and J. M. Borrego, *J. Electrochem. Soc.* **117**, 688 (1979).