

# Lattice Monte Carlo simulations as link between ab-initio calculations and macroscopic behavior of dopants and defects in silicon

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In this work, we show that lattice Monte Carlo simulations can be used to span the time and distance scales between underlying atomistic processes and macroscopic diffusion behavior. We use *ab-initio* calculations of binding energies versus configuration to calculate hopping rates of vacancies for use in lattice Monte Carlo (LMC) simulations of diffusion and aggregation in silicon. The LMC simulations consider the biased nature of vacancy hop frequencies in the neighborhood of dopants, with interactions up to sixth-nearest-neighbor distances included. We use these simulations to investigate the expected macroscopic diffusion behavior, as well as the process by which dopant/defect aggregation occurs. Specific phenomena investigated include collective behavior leading to greatly enhanced diffusivity at high doping levels, the time dependence of effective diffusivity due to the formation of dopant/vacancy clusters, and dopant fluxes in the presence of a vacancy gradient.

## INTRODUCTION

Observable macroscopic behavior such as impurity diffusion and aggregation depend on the underlying atomic-level processes. Recently it has become possible to use *ab-initio* calculations based on density functional theory (DFT) and the local density approximation (LDA) to investigate these atomic-scale processes. As an example that we will apply in this work, the binding energies for dopants, vacancies and related clusters in silicon have been calculated as functions of the local configuration by several groups<sup>1,2,3</sup> (Fig. 1). In contrast with simple pair diffusion models which provide the basis for most continuum modeling, these calculations show that relatively long-range interactions exist between dopants and vacancies (out to at least tenth nearest neighbor distances). The presence of long-range interactions opens the door for relatively complex interactions among multiple dopants with multiple vacancies, particularly at high doping levels. In order to explore how the nature of these dopant/vacancy interactions controls macroscopic diffusion and aggregation behavior, we apply a lattice Monte Carlo (LMC) approach<sup>5</sup>. The underlying concept is that the fundamental processes involved in diffusion in a crystalline material are the hopping of mobile species (defects) between lattice sites. In our case, the mobile species are vacancies which displace either lattice or dopant atoms as they move. By considering only the defects (vacancies) rather than every lattice atom and only the hops rather than each vibration, a huge reduction in computational requirements can be achieved in comparison with molecular dynamics. Thus it is possible to simulate large systems ( $10^8$  atoms) and long times (seconds) while still including the critical atomic scale processes and interactions.

## DISCUSSION AND RESULTS

In our LMC simulations, we use periodic boundary conditions on a three-dimensional (3D) array of cubic cells, each with 8 lattice sites as in the silicon (or diamond) structure.

Dopant/vacancy interactions are specified in terms of energy as a function of atomic configuration. Interaction energies are assumed to be additive, an assumption which is close to what is found by first-principle calculations<sup>3</sup>. To initialize the system, dopants are placed randomly within the 3D structure according to the designated doping density. The vacancies are then placed with the probability of occupation depending on the binding energy for each site as calculated based on the dopants in the neighboring region:

$$p_V = \frac{p_V^0}{p_V^0 + (1 - p_V^0) \exp(\Delta E/kT)} \quad (1)$$

where  $p_V^0$  is the probability of occupation for sites far from any dopant atom,  $k$  is Boltzmann's constant and  $T$  is the absolute temperature. The energy  $\Delta E$  is:

$$\Delta E = - \sum_{i=1}^n n_i \Delta E_i, \quad (2)$$

$n_i$  being the number of dopant atoms as  $i^{\text{th}}$ -nearest neighbor and  $\Delta E_i$  the corresponding dopant/vacancy binding energy. We consider values of  $n$  between 3 and 6 in this work, since as recognized by Hu<sup>6</sup>, long range migration of a dopant via vacancy-mediated diffusion requires separation to the third-nearest neighbor (3NN) site with respect to a dopant, while the long-range migration of an  $\text{As}_2\text{V}$  complex requires dopant/vacancy separation to a 6NN distance. The following values for the arsenic/vacancy binding energies are used from the *ab-initio* calculations of Pankratov<sup>1</sup>: 1.19 eV for the first-nearest neighbor (1NN), 0.50eV for the second-nearest neighbor (2NN), 0.41eV for the 3NN, 0.39eV for 4NN, 0.37eV for 5NN, and 0.33 for 6NN.

The system evolves by considering the hopping of vacancies (actually the hopping of adjacent atoms onto the vacant site) with transition rates biased by the change in the system energy ( $\Delta E_{\text{final}} - \Delta E_{\text{initial}}$ ) associated with the prospective exchange:

$$\nu = \nu^0 \exp\left(-\frac{\Delta E_{\text{final}} - \Delta E_{\text{initial}}}{2kT}\right) \quad (3)$$

where  $\Delta E_{\text{initial}}$  and  $\Delta E_{\text{final}}$  are calculated using Eq. (2) and represent the energies before and after the prospective transition, respectively. At each step, we update the hopping rates for vacancies, choose a hop based on the relative rates, and increment the time. In the end, the mean squared displacement is calculated to obtain the diffusivity.

The first problem we will consider is the diffusion of dopants at very high concentrations, for which seemingly anomalous behavior has been observed. Rapid thermal annealing (RTA) experiments by Larsen<sup>7</sup> made at 1050°C for 10 seconds indicate that below a threshold concentration ( $\sim 2 \times 10^{20} \text{ cm}^{-3}$ ), the diffusivity of group IV and V impurities (As, Sb, Sn and Ge) increases linearly with dopant concentration, while above this concentration the diffusivity increases dramatically with increasing donor concentration ( $\propto C^n$ ,  $n \sim 3 - 6$ ). Earlier investigations<sup>8</sup> carried out over longer times (several hours) found that in the temperature range 1000–1100°C, the diffusivity of dopants (As) decreases rather than increases at very high concentration.

Previous calculations<sup>4,5</sup> using rough estimates of dopant/vacancy binding energies provided good agreement with the experimental observations of Larsen<sup>7</sup>, predicting both the doping level at which the onset of enhanced diffusion occurs and as well as the dependence

of diffusivity on increasing concentration. Using parameters from *ab-initio* calculations in the framework of 3NN interactions, we again find a strong enhancement in diffusivity for high doping levels and short simulation times (see Fig. 2, noting that Fermi level effects have been normalized out). However, we find that at longer simulation times, the diffusivity enhancement decreases substantially (see Fig. 3), in agreement with experimental observations at longer times<sup>8</sup>, the phenomenon being more pronounced at high doping levels.

To understand this behavior we examined the evolution in the number of  $\text{As}_x\text{V}$  complexes in the system (see Figs. 4(a) and 4(b)). The role of  $\text{As}_x\text{V}$  complexes in the overall diffusion process has been discussed recently by Ramamoorthy and Pantelides<sup>3</sup>. Based on their calculations, they proposed  $\text{As}_2\text{V}$  to be mobile and to have a significant role in the dopant diffusion. What we find from LMC simulations is that because of the strong dopant/vacancy binding, at high doping levels the number of  $\text{As}_2\text{V}$  complexes is higher than the number of  $\text{AsV}$  pairs and that their number grows with time, while the number of pairs decreases. As time progresses larger clusters such as  $\text{As}_3\text{V}$  and  $\text{As}_4\text{V}$  supplant the  $\text{As}_2\text{V}$  complexes. Since the larger complexes are much less mobile than the pairs, this is the source of the diffusivity reduction observed in our simulations. To investigate further the role of  $\text{As}_2\text{V}$  complexes, we extended the dopant-vacancy interactions considered up to the sixth-nearest-neighbor (6NN) distance, since for long-range diffusion of the  $\text{As}_2\text{V}$  it is necessary for the vacancy to move away until it is at distances of 3NN and 6NN from the two dopants, respectively. By examining the motion of isolated complexes (e.g., a one vacancy, two arsenic atom system), we find that the diffusivity of  $\text{As}_2\text{V}$  complexes is about 50 times smaller than that of pairs at 900°C. However, as seen in Figs. 4(a) and 4(b), at high doping level the number of  $\text{As}_2\text{V}$  complexes greatly exceeds that of pairs, so these complexes can have a significant role in diffusion. In fact by combining the equilibrium concentrations of complexes with their diffusivity, we find that for a concentration of  $10^{20}\text{cm}^{-3}$  at 900°C, the contribution of  $\text{As}_2\text{V}$  to diffusion exceeds that of pairs (Fig. 5). However, a transition from diffusion dominated by pairs to domination by  $\text{As}_2\text{V}$  leads only to an increase of one in the order of the diffusivity increase with doping, in contrast to the much more abrupt increase observed both experimentally and in LMC simulations. Thus, although mobile complexes may play a significant role at high concentrations, the rapid increase in diffusivity with doping at very high levels is due predominantly to collective effects involving the interactions of vacancies with multiple nearby dopant atoms.

We have also applied the LMC approach to study diffusion at moderate doping levels. In particular, we examined the flux of dopants resulting from a gradient in the vacancy concentration. While pair diffusion theories predict a flux of dopants in the same direction as the flux of vacancies, other simple vacancy mechanism predicts the the dopant flux to be in the opposite direction<sup>9</sup> based on the fact that in any exchange, the vacancy and dopant atom move in opposite directions. We can write a general expression for dopant flux spanning both these models as:

$$J_A^V = -D_{AV}K_{A/V}(C_V\nabla C_A + \gamma C_A\nabla C_V). \quad (4)$$

For ideal pair diffusion, the value of  $\gamma$  should be equal to one, while for simple displacement by vacancies,  $\gamma = -2$ <sup>10</sup>.

We performed a series of simulations with and without vacancy gradients and found  $\gamma$  for arsenic and phosphorus at different temperatures for moderate doping levels. We find that the fluxes of dopants and vacancies are in the same direction ( $\gamma > 0$ ). However, for

arsenic, we find that  $\gamma$  is less than one in agreement with calculations by List<sup>10</sup> as well as our previous work<sup>5</sup>, and that  $\gamma$  decreases with temperature (see Fig. 6). In contrast, for phosphorus, we find that  $\gamma$  converges to one, independent of temperature (see Fig. 7). One can understand this behavior by considering the mechanism for vacancy-mediated diffusion. Vacancies are most likely to initially approach arsenic atoms from the direction of higher concentration, leading to initial exchanges biased up the vacancy gradient ( $\gamma < 0$ ). However, due to the long-range dopant/defect binding, the arsenic and vacancy are likely to diffuse as a pair for some number of hops, resulting in a flux from regions of high to low vacancy (and thus also pair) concentration ( $\gamma > 0$ ). A very tightly bound pair would be expected to make many hops and thus overwhelm any influence of the initial hop, giving  $\gamma = 1$ . At higher temperatures, it is easier for pairs to dissociate so fewer hops can be expected before a pair breaks up. This leads to a greater influence of the initial hop and thus a smaller value for  $\gamma$  as seen in the simulations. In the case of phosphorus, the large dopant/vacancy exchange barrier eliminates the initial bias in the hop direction. A captured vacancy is likely to separate many times to 3NN sites, with the potential each time to return along a different path, before a dopant vacancy exchange takes place. Thus  $\gamma \Rightarrow 1$ .

## CONCLUSIONS

In conclusion, we have used values for dopant/vacancy binding energies versus distance from *ab-initio* calculations<sup>1,2,3</sup> in lattice Monte Carlo simulations of vacancy-mediated diffusion in silicon. As observed experimentally<sup>7</sup>, we found a strong diffusivity enhancement for arsenic in heavily doped silicon. Our results also show that arsenic clustering takes place for longer times, again in agreement with experiments<sup>8</sup>. The role of mobile As<sub>2</sub>V complexes was also explored, leading to the conclusion that these complexes are in fact mobile and can contribute significantly to diffusion, although their diffusivity is much smaller than the diffusivity of pairs, since they are present in higher numbers at high doping levels. However, the large enhancement in diffusivity at high doping levels is due primarily to collective effects involving the interactions of vacancies (even those in complexes) with several dopant atoms.

We also found that for arsenic, the dopant flux in a vacancy gradient is smaller than that predicted by pair diffusion theory and decreases with increasing temperature. In the case of phosphorus, we found the dopant flux to match that predicted by pair diffusion, with the difference attributed to the fact that pair migration is limited by dopant/vacancy exchange, rather than separation to third-nearest neighbor distances as for arsenic.

## REFERENCES

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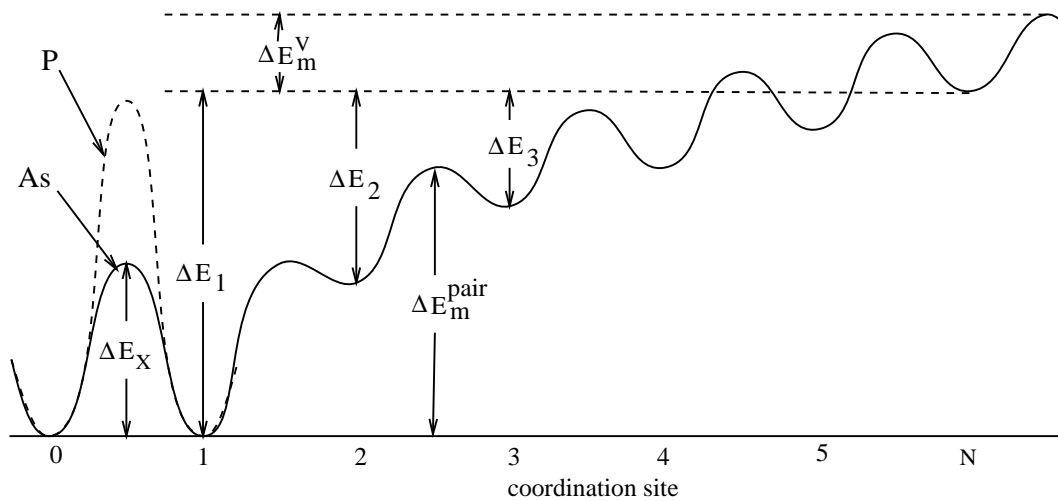
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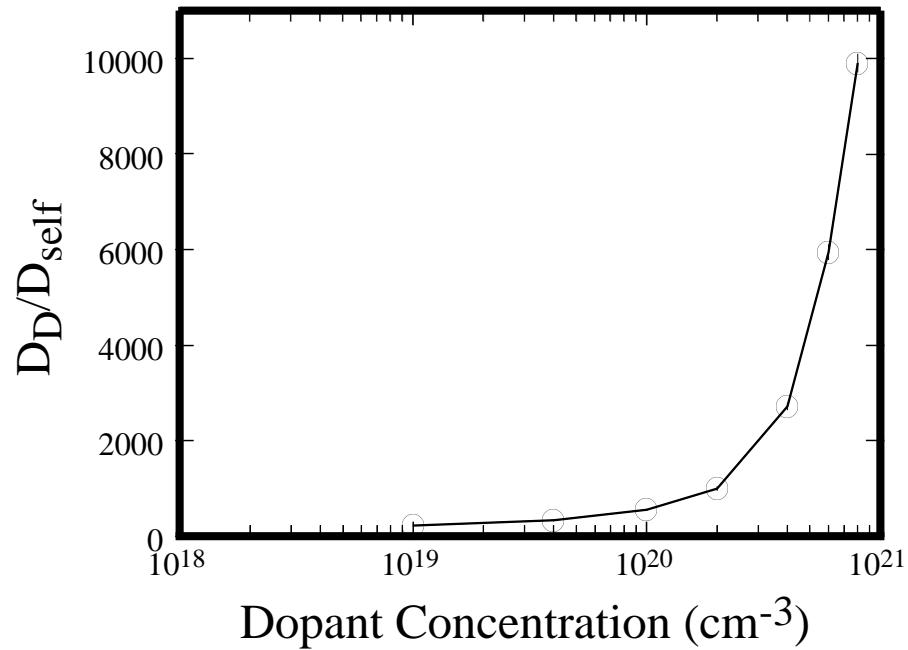
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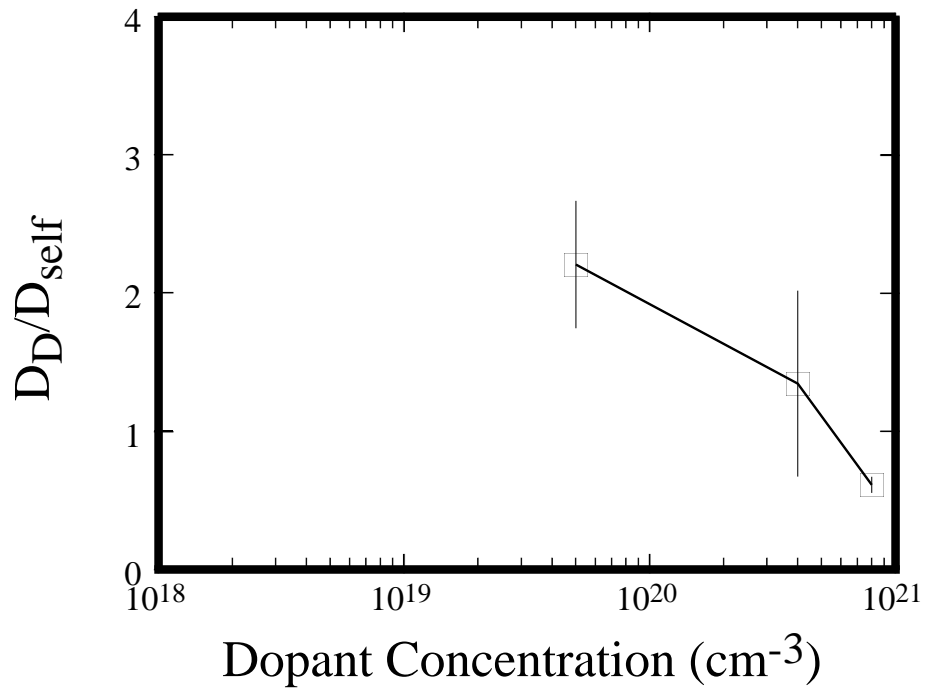
<sup>10</sup>See S. List, P. Pichler and H. Ryssel, 1996 Int'l Conf. on Simulation of Semiconductor Processes and Devices. SISPAD '96, **27-8**, 184 (1996) and references therein.



**Figure 1:** Schematic illustration of dopant/vacancy binding energy as a function of position based on the *ab-initio* calculations of Pankratov<sup>1</sup> and Nelson<sup>2</sup>. The potential barriers for arsenic/vacancy and phosphorus/vacancy exchange as well as pair migration are also shown.

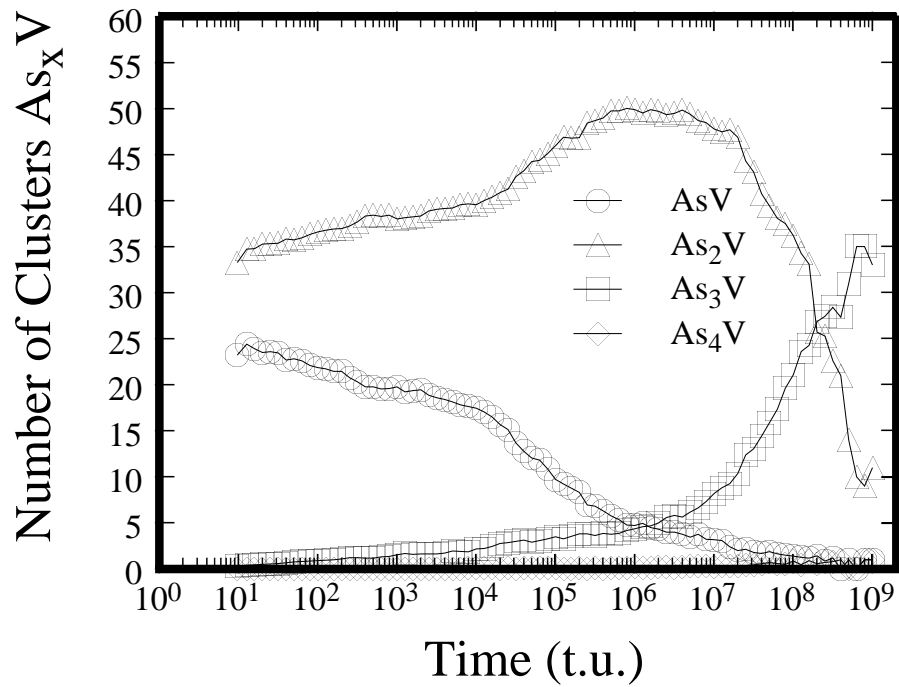
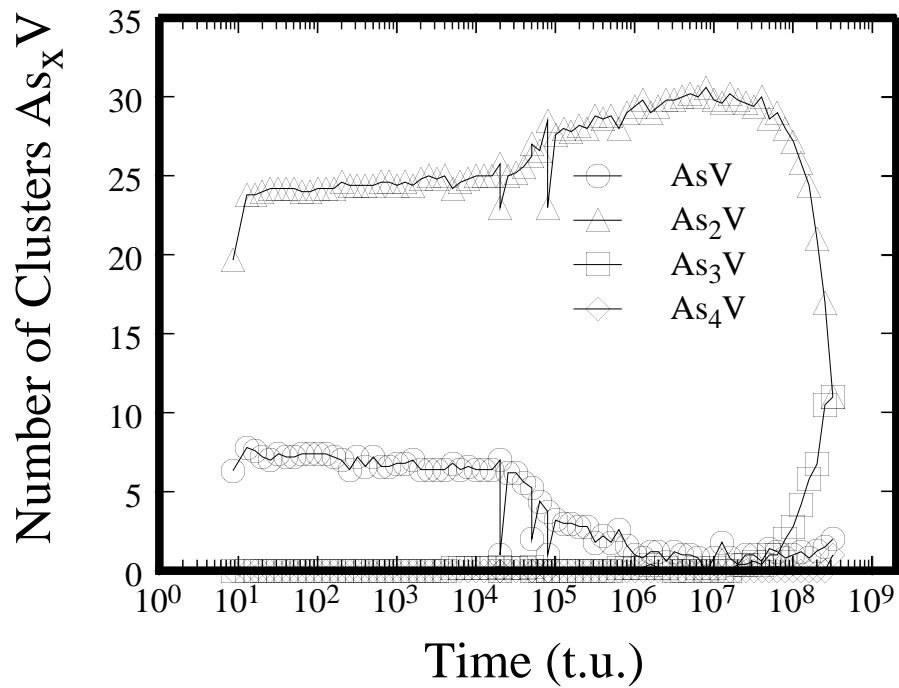


**Figure 2:** Normalized arsenic diffusivity versus doping density at 900°C from LMC simulations using *ab-initio* parameters <sup>1,2</sup> after 10<sup>4</sup> t.u. 1 t.u. = 1/ν<sup>0</sup> where ν<sup>0</sup> is the hopping frequency of a free vacancy. Note the strong increase above C = 2 × 10<sup>20</sup> cm<sup>-3</sup>. The normalized diffusivity obtained by dividing by the vacancy component of silicon self-diffusion (D<sub>v</sub>C<sub>v</sub><sup>\*</sup>), thus removing the Fermi level dependence.

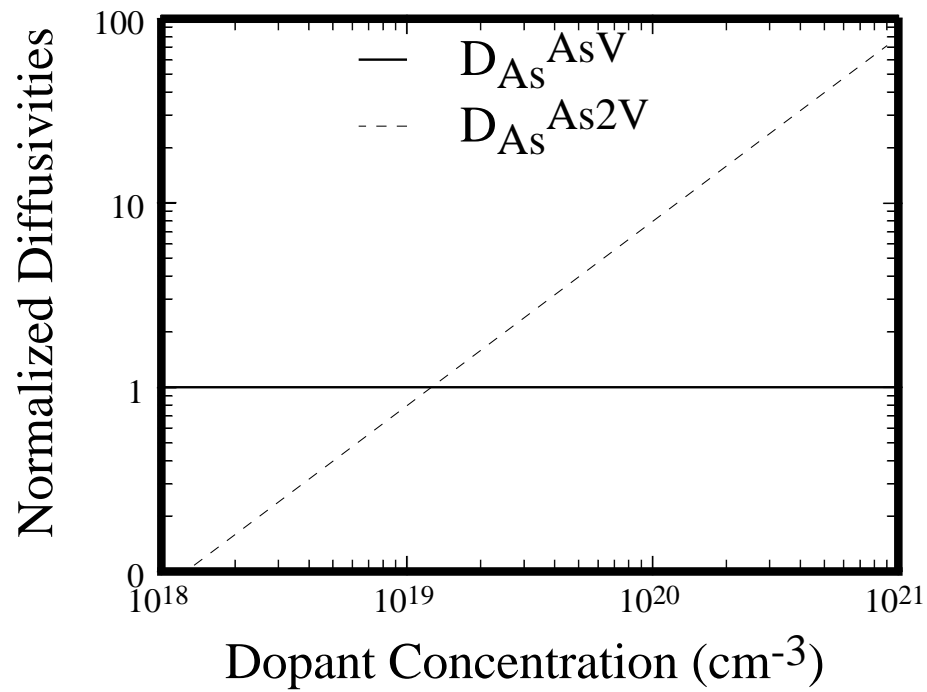


**Figure 3:** Normalized arsenic diffusivity versus doping density at 900°C from LMC simulations using *ab-initio* parameters <sup>1,2</sup> after  $10^9$  t.u. . The diffusivity actually drops rather than increasing as in Fig. 2 due to clustering.

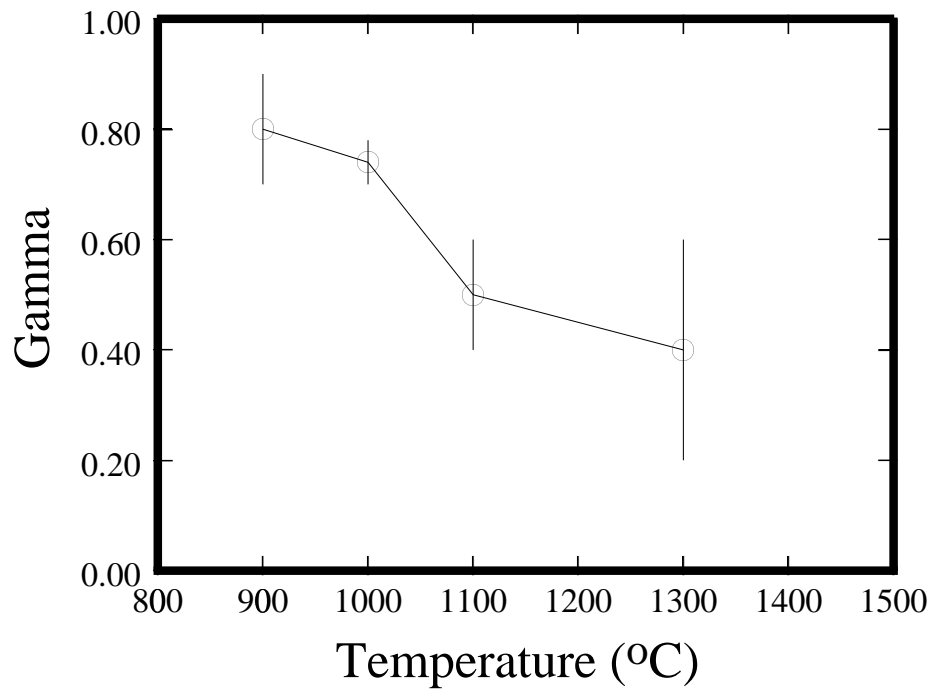




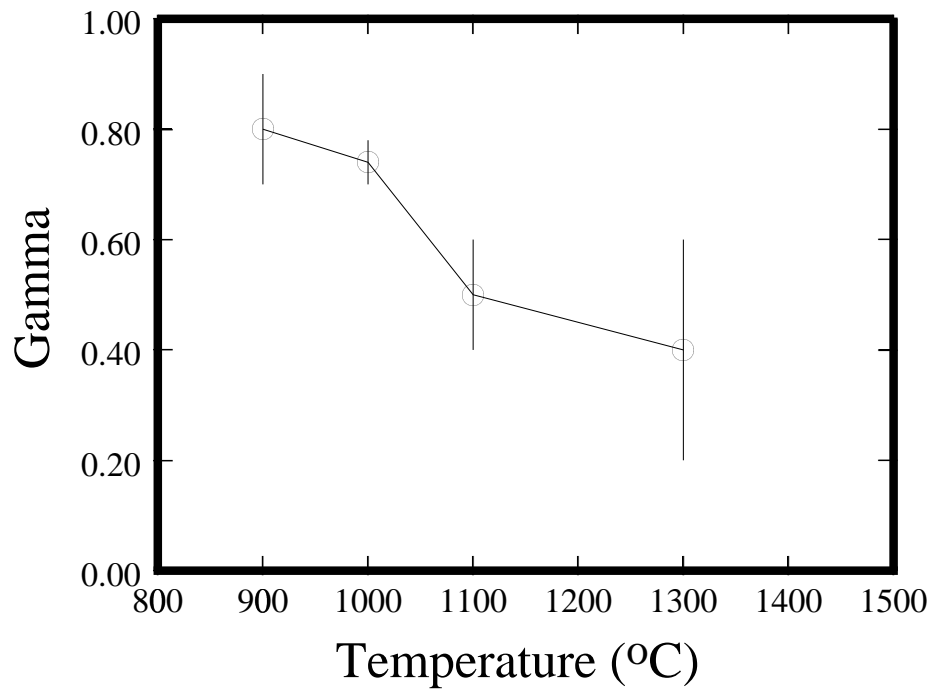
**Figure 4:** Number of  $As_xV$  clusters versus simulation time at  $900^\circ C$  a) for dopant density of  $5 \times 10^{19} cm^{-3}$  and b) for dopant density of  $4 \times 10^{20} cm^{-3}$ .



**Figure 5:** Relative diffusivities of arsenic due to AsV pairs and As<sub>2</sub>V complexes versus doping level at 900°C. The contribution of As<sub>2</sub>V to diffusion is predicted to dominate above  $C_{\text{As}} = 2 \times 10^{19} \text{cm}^{-3}$ .



**Figure 6:** Transport coefficient  $\gamma$  versus temperature for arsenic 900°C in the presence of a vacancy gradient.



**Figure 7:** Transport coefficient  $\gamma$  versus temperature for phosphorus at 900°C in the presence of a vacancy gradient.