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Dopant-vacancy cluster formation in germanium

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Recent experimental and theoretical studies revealed that dopants in germanium (Ge) cluster with lattice vacancies (V). The existence of these larger clusters has been recently predicted and is important as they can contribute to the low activation of dopants in Ge. With the use of electronic structure calculations we study the binding energies of clusters formed with the association of dopant atoms and vacancies. As an example of the kinetics of such clusters the diffusion of two phosporous-vacancy ($P_2 V$) clusters via the ring mechanism of diffusion in predicted. These $P_2 V$ clusters are important as they can act as precursors for the formation of the larger $P_3 V$ and $P_4 V$ clusters. The present study provides information on the structure of clusters and is consistent with recent experimental results, which indicate that the formation of clusters in heavily doped Ge is possible. In agreement with experiment, we predict that the diffusion of $P V$ pairs is retarded by the addition of a further P atom. © *2010 American Institute of Physics*. [doi:10.1063/1.3361115]

Ge has the potential to replace silicon (Si) in advanced nanoelectronic devices because of its higher mobility of holes and electrons, compatibility with Si manufacturing processes, increased dopant solubility, and smaller band gap.[1] For the fabrication of Ge-based devices, it is important to form shallow junctions with high electrically active dopant concentrations. The absolute control required for these processes necessitates the determination of the migration properties of dopants in Ge.[2] This is particularly important for dopants such as P or arsenic (As) that present problematic diffusion and activation control.[3,4] In recent studies, it has been concluded that self and dopant atom diffusion in Ge is mainly described on the basis of the V-mechanism.[2,5–8] The formation of clusters containing two dopant atoms surrounding a V has been recently observed.[7] These are important as they can act as precursors for the formation of larger $D_n V_m$ clusters. The formation of $D_n V_m$ clusters can lead to the trapping of charge in the cluster, therefore the donor atoms do not donate their electron nor do the acceptor atoms accept their electron from the Ge lattice. This may lead to the deactivation of a significant part of the total dopant dose. The formation and relative concentrations of the larger $D_n V$ clusters have been recently predicted with the use of density functional theory (DFT) and mass action analysis.[9–11] For heavily phosphorous-doped Ge secondary ion mass spectroscopy (SIMS) measurements reveal that a significant amount of the dose is trapped in characteristic humps, which have been attributed to clustering.[4,12] For other technologically important such as boron (B), aluminum (Al), gallium (Ga), indium (In) carbon (C), Si, nitrogen (N), and antimony (Sb), there are only a few studies investigating their clustering and diffusion (for example Refs. 2, 6, and 7 and references therein). The aim of this study is to compare the migration energy barriers of $P V$ pairs and $P_2 V$ clusters, suggest a

mechanism for $P_2 V$ diffusion and calculate the binding energies of dopant-vacancy clusters for a range of dopants.

Plane-wave DFT with a plane-wave basis set with an energy cut off of 350 eV was used. The generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof[13] exchange-correlation functional in conjunction with ultrasoft pseudopotentials[14] was implemented. All the simulations were performed using the CASTEP code.[15,16] A supercell containing 64 diamond structure tetrahedral sites was used to describe Ge. Brillouin-zone sampling was used with a Monkhorst–Pack[17] grid of $2 \times 2 \times 2$ k-points. The efficacy of the present methodology to describe the dopant-defect interactions in Ge and related materials was demonstrated in recent studies[6,9,18–21] in comparison with experiments.[2,7] The linear synchronous transit (LST) method was implemented to inspect the migration energy barriers.[22,23] The LST method has been recently applied to study the migration of dopant atoms in Si, SiGe, and Ge.[9,24,25]

DFT calculations based upon the GGA (or the local density approximation) underestimate the formation energies of defects in Si and Ge, due to the appropriate representation of exchange in these functionals.[26,27] For this reason, this communication is mainly focused on binding energies (differences in energy) and clusters in their neutral charge state as these are expected to be less sensitive to systematic errors in the exchange-correlation energy. Regarding the $P_2 V$ cluster it was recently predicted[8] that the migration of the $P_2 V$ cluster is not affected by the charge state. On the contrary, for DV pairs, $D \varepsilon$ {P, As, Sb}, the most recent experimental studies determined that they are negatively charged.[2,7] In the present study, we will use the predicted value of Uberuaga *et al.*[28] of 2.4 eV for the V formation enthalpy (H_V^f).

When a V encounters a D atom the latter can move onto the vacant site and the V simultaneously in the opposite direction. However, these events were the D and the V simply exchange positions do not effectively lead to the absolute displacement of the D atom. For the net displacement of a D in the Ge lattice the V must move away to at least the third-

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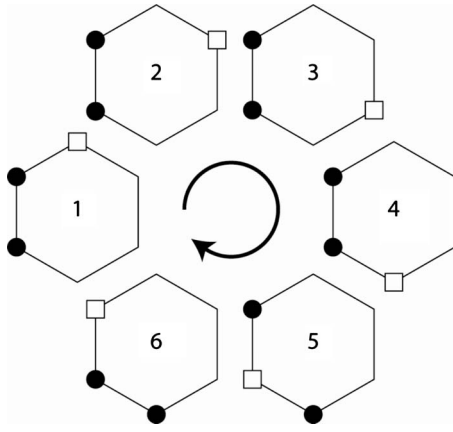
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FIG. 1. A schematic view of the ring mechanism of diffusion of the $P_2 V$ pair (P=black circles and V=squares) projected onto the (111) surface of Ge.

FIG. 2. The migration energy profile of the $P_2 V$ cluster in Ge.

nearest neighbor site and return along a different path. This is known as the ring mechanism for diffusion[29,30] (see, for example, Fig. 1 of Ref. 6). In the present work, we consider a similar ring mechanism for the $P_2 V$ clusters (see Fig. 1). In particular the V moves away from the PP pair and returns along a different path (see Fig. 1).

The $P_2 V$ clusters form due to the attractive nature between V and P. The most stable configuration is with the V in the middle surrounded by two first nearest neighbor P atoms P V P (Fig. 1 (5), Table I). Here negative binding enthalpies [defined as $E_b = E_{defect\text{-}cluster} - (\Sigma E_{isolated\text{-}defects})$] represent stable clusters with respect to isolated defects. Figure 2 represents the migration energy barriers of the $P_2 V$ clusters in Ge. The greatest migration energy predicted is the exchange between the P atom and the V [i.e., in Figs. 1 and 2 the step from (5) to (6)]. This migration energy barrier is 1.88 eV in excellent agreement with the value of 1.8 eV of a recent study.[8] In that study, Janke[8] used a local density functional code, near-spherical clusters of Ge atoms terminated by hydrogen atoms, whereas the migration energies and paths were calculated using the nudged elastic band method. The agreement of the two approaches indicates the accuracy of the predicted migration energy barrier.

The migration energy barriers for the $P_2 V$ clusters in Ge are higher compared to the P V pairs by 0.78 eV (compare Table I with Ref. 6). We also calculated the activation enthalpy, Q_a, using

$$Q_a = H_V^f + \Delta E_{P\,V\,P} + H_{P_2\,V}^m, \qquad (1)$$

where $\Delta E_{P\,V\,P}$ is the binding energy of the most stable configuration and $H_{P_2\,V}^m$ is the greatest migration enthalpy barrier (See Fig. 2 and Table I). The predicted activation enthalpies

is 3.22 eV for $P_2 V$ and is higher by 0.24 eV compared to the P V (compare Table I with Ref. 6). This hints that the $P_2 V$ clusters will be less mobile compared to the P V pairs consistently with recent experimental results.[7]

This in turn will imply that even if the $P_2 V$ clusters form, the formation of the larger $P_n V$ clusters, whose existence was predicted recently,[10] will be kinetically hindered. Nevertheless, under certain doping conditions these larger clusters may become important, as predicted by recent studies.[9–11] For comparison, in Si previous theoretical[31] and experimental[32] results predict that $As_2 V$ clusters will be less mobile compared to As V pairs but the formation of the larger $As_n V$ clusters has been observed especially in heavily As doped Si.[31,32] In Ge, the experiments of Brotzmann *et al.*[7] determined that the $P_2 V$, $As_2 V$, and $Sb_2 V$ clusters are less mobile than the P V, As V, and Sb V pairs, respectively. It cannot be excluded that other more complex mechanisms can lead to the formation of clusters. For example, it might be the case that $D_n V$ form via only the mobile DV pairs with the extra V diffusing away.

Is the formation of $D_n V$ clusters limited to donor atoms such as P in Ge? To address this issue, we report the binding energies of DV, VDD [see Fig. 1 (1)] and DVD [see Fig. 1 (5)] clusters for eleven dopants (see Table II). Notably, apart

TABLE II. Predicted binding enthalpies for DV, VDD [see Fig. 1 (1)], and DVD [see Fig. 1 (5)] clusters (in electron volt).

Dopant (D)	DV	VDD	DVD
B	0.32[a]	0.35	0.65
Al	−0.40[b]	−0.40	−0.38
Ga	−0.15[b]	0.06	−0.31
In	−0.96[b]	−1.42	−1.40
C	−0.07[a]	−0.03[d]	−0.24[d]
Si	0.24[b]	0.23	0.50
Sn	−0.64[b]	−1.00	−0.97
N	−1.05[c]	−1.22[c]	−2.20[c]
P	−0.52[a]	−0.55	−1.06[e]
As	−0.60[a]	−0.65	−1.22[e]
Sb	−0.70[b]	−0.91	−1.40[e]

[a]Reference 19.
[b]Reference 6.
[c]Reference 39.
[d]Reference 38.
[e]Reference 9.

TABLE I. Predicted binding $\Delta E_{P\,V\,P}$ for the P V P configuration [see Fig. 1 (5)], $\Delta E_{P_2\,V}^1$ [see Fig. 1 (1)] $\Delta E_{P_2\,V}^2$ [see Fig. 1 (2) or (3)], and migration enthalpies ($H_{P_2\,V}^m$) for the $P_2 V$ clusters (in electron volt).

Defect complex	$\Delta E_{P\,V\,P}$	$\Delta E_{P_2\,V}^1$	$\Delta E_{P_2\,V}^2$	$H_{P_2\,V}^m$
$P_2 V$	−1.06	−0.55[a]	−0.21	1.88

[a]Reference 9

from boron and silicon all other dopants form negative binding energy DV and D_2V clusters. The instability of boron-vacancy clusters is consistent with the recent experimental evidence that boron has high activation energy of diffusion in Ge.[33] Bruno *et al.*[34] determined that boron is mobile under proton irradiation but its diffusion occurs via the kick-out process and not by a vacancy-mechanism as in the case of P, As or Sb atoms in Ge.

Si V pairs are not stable (0.24 eV, see Table II) in Ge as Si is isovalent and smaller and therefore there is no energy gain of positioning it next to a V. Conversely, the binding energy of a Ge V pair in Si is -0.27 eV and can be attributed mainly to the relaxation allowed when the larger Ge atom is at a nearest neighbor site to the V.[35]

Apart from B all the other acceptor dopants considered (Al, Ga, and In) are predicted to form stable dopant-vacancy clusters. Interestingly, two very recent experimental studies attribute the deactivation of Ga and indium in Ge on cluster formation.[36,37] For example, Kube *et al.*[36] used SIMS to investigate heavily indium implanted Ge samples. It was determined that a significant amount of the indium dose was trapped in a characteristic hump that resembles the profiles previously reported for phosphorus implanted Ge.[12,36]

The C V pair is only barely bound, however, in recent work the importance of clustering when carbon was codoped with Sn, P, As, or Sb atoms was highlighted.[7,9,38] Interestingly, codoping with C leads to the retardation of the P V, As V, and Sb V pairs,[7,9] whereas the C V Sn cluster is very stable (binding energy -1.48 eV).[38]

Importantly, N forms the most bound cluster (N V N) with a binding energy of -2.20 eV (see Table II and Ref. 37). Therefore, the presence of N in Ge could lead to the formation of N-vacancy clusters, thus affecting the concentration of unbound V that will be available to bind with dopants. This could in turn affect the diffusion of dopants such as P, As, and Sb that diffuse with the V-mediated mechanism. The DVD clusters are significantly more bound than the VDD clusters for Ga, C, N, P, As, and Sb. For Al, In, and Sn the binding energy differences between the two configurations are very small (within 0.03 eV, see Table II).

In summary, the present DFT results are consistent with previous experiments and support the picture of cluster formation in Ge for most dopants considered. These clusters may explain the deactivation of dopants under high concentration conditions. Monte Carlo simulations are necessary to predict in detail the mechanism of formation and the kinetics of the larger deactivating clusters. Charged defects, however, can be important in semiconductors but we expect that important trends can also be observed by comparing neutral defects.[6,39,40] The importance of negatively charged DV pairs, for $D \, \varepsilon \, \{P, As, Sb\}$, was recently determined in Ge under extrinsic doping conditions.[1,2,41] In particular the observed box-shaped concentration-depth profiles (characteristic of concentration dependent diffusion), under extrinsic doping conditions, were explained by the use of singly negatively charged DV pairs.[2,41]

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