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Vacancy-mediated dopant diffusion activation enthalpies for germanium

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Electronic structure calculations are used to predict the activation enthalpies of diffusion for a range of impurity atoms (aluminium, gallium, indium, silicon, tin, phosphorus, arsenic, and antimony) in germanium. Consistent with experimental studies, all the impurity atoms considered diffuse via their interaction with vacancies. Overall, the calculated diffusion activation enthalpies are in good agreement with the experimental results, with the exception of indium, where the most recent experimental study suggests a significantly higher activation enthalpy. Here, we predict that indium diffuses with an activation enthalpy of 2.79 eV, essentially the same as the value determined by early radiotracer studies. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2918842]

Germanium (Ge) has the potential to replace silicon (Si) in advanced nanoelectronic devices because of the higher mobility of holes and electrons, compatibility with Si manufacturing processes, increased dopant solubility, and smaller band gap.[1] The precise control required for the fabrication of these devices would be greatly aided by an accurate determination of the diffusion properties of impurities in Ge.[2] This is particularly important for donor impurities for which activation control can be problematic.[3] In previous studies, it has been concluded that most impurities mainly occupy substitutional lattice sites in Ge and, with the exception of boron (B), dopant diffusion is mainly mediated by vacancies (V) as interstitial mechanisms typically have significantly higher activation enthalpies.[2,4–25]

Aluminium (Al), gallium (Ga), indium (In), and B are acceptor atoms that can potentially be used as p-type dopants in Ge technology. Recent experiments[4] on B diffusion in Ge yield an activation enthalpy of 4.65 eV that agrees with earlier results, but the absolute values of the B diffusion coefficients are several orders of magnitude lower than those reported earlier.[5] Previous experimental studies on Al diffusion yield activation enthalpies in the range of 3.2–3.45 eV.[6,7] Södervall *et al.*[8] obtained an activation enthalpy of 3.31 eV for Ga diffusion in Ge. This value is supported by the more recent experimental studies of Riihimäki *et al.*[9] who determined an activation enthalpy of 3.21 eV for Ga diffusion in Ge via a V-mediated mechanism. The spread in the data reported for the activation enthalpy of In diffusion in Ge is especially large (0.85 eV). The radiotracer studies of Pantaleev[10] suggest a value of 2.78 eV, whereas the In profiles measured by Dorner *et al.*[11] by means of secondary ion mass spectrometry (SIMS) yield a value of 3.63 eV.

Carbon (C), Si, and tin (Sn) are important isovalent impurities. C atoms have been observed to be relatively immobile; however, they can retard the diffusion of phosphorus (P), arsenic (As), and antimony (Sb) atoms in Ge.[26,27] Recent experimental studies by Silvestri *et al.*[15] (using SIMS) concluded that Si diffusion in Ge is mediated by V with an activation enthalpy of 3.32 eV, whereas previous studies determined values in the range of 2.9–3.47 eV.[12–14] The diffusion of Si in Ge is slower than Ge self-diffusion.[13,15] The slightly higher activation enthalpy for Si diffusion compared to self-diffusion is consistent with a V-mechanism.[15] Sn was recently determined to diffuse in Ge via the V-mediated mechanism with an activation enthalpy of about 2.9 eV.[9] Earlier studies suggest values in the range of 3.05–3.26 eV.[20–22]

All donor atoms considered in this work (P, As, and Sb) diffuse via their interaction with lattice V.[1,2,7,9] Recent diffusion experiments[2] indicate that the activation enthalpy for diffusion decreases with increasing donor size (2.85 eV for P, 2.71 eV for As, and 2.55 eV for Sb). This trend was not observed in the early studies of Dunlap[23] and Karstensen,[24] probably because of the limited accuracy of the applied p-n-junction method.

The aim of this study is to use density functional theory (DFT) to predict the activation enthalpies of diffusion for a range of impurity atoms (Al, Ga, In, Si, Sn, P, As, and Sb) and compare them to previous experimental results.

For all calculations, DFT with a plane-wave basis set with an energy cutoff of 350 eV was used. The generalized gradient approximation using the Perdew–Burke–Ernzerhof[28] exchange-correlation functional in conjunction with ultrasoft pseudopotentials[29] was employed. The calculations were performed with the CASTEP code.[30,31] A 64 atom supercell was used (under zero pressure conditions) as well as Brillouin-zone sampling with a Monkhorst–Pack[32] grid of 2^3 k-points. The atoms were allowed to relax by using energy minimization. Adequate convergence of these computational parameters was previously demonstrated.[33,34]

DFT calculations underestimate the formation energies of defects in Si and Ge due to the lack of exact exchange in the functionals.[35,36] A way to overcome this problem is the application of an alternative functional, such as the B3YLP, as previously discussed by Uberuaga *et al.*[35] In the present study, we will use the predicted values of Uberuaga *et al.*[35] of 2.4 and 0.7 eV for the formation and migration enthalpies, respectively, of a V in Ge. Adding these values gives an activation enthalpy of self-diffusion via V of 3.1 eV. This value is in excellent agreement with the activation enthalpy of 3.09 eV experimentally determined by Werner *et al.*[18] for Ge self-diffusion. The pressure dependence of Ge diffusion

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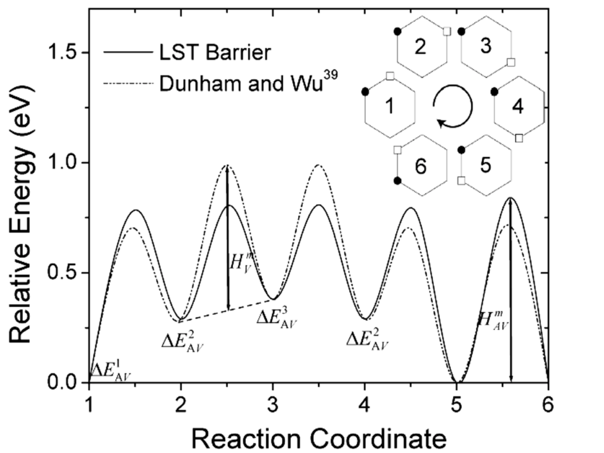

FIG. 1. (Color online) The idealized Dunham and Wu (Ref. 39) path compared to the path calculated by using LST simulations to estimate the migration energy of the V with respect to an As atom. The inset represents the ring mechanism of diffusion for the AsV pair (As=black circles and V=squares) projected onto the (111) surface of Ge.

and the diffusion behavior of copper in Ge (Refs. 16 and 17) indicate that self-diffusion in Ge is primarily V-mediated. The accuracy of the self-diffusion data reported by Werner *et al.*[18] has been recently verified by Schneider *et al.*[19]

Other enthalpies required to describe dopant diffusion in Ge are binding enthalpies [defined as $E_b = E_{\text{defect-cluster}} - (\Sigma E_{\text{isolated-defects}})$]. These are expected to be less sensitive to the exchange-correlation functional, as discussed in previous studies.[34,37] A negative binding enthalpy implies that the defect cluster is stable with respect to its constituent point defect components. Migration enthalpy barriers between stable configurations are also needed as discussed below.

If a V encounters a dopant atom, the latter moves onto the vacant site and the V is translated in the opposite direction. Such repeated exchanges, where the dopant and the V simply swap place, do not lead to the net displacement of the dopant atom. For the displacement of a dopant through Ge, the V must move away to at least the third nearest neighbor site and return along a different path. This is the ring mechanism for diffusion[38] and is represented in the inset of Fig. 1.

In an analysis of V-mediated diffusion in a diamond structure, Dunham and Wu[39] defined the activation enthalpy of diffusion, Q_a, as

$$Q_a = H_V^f + H_V^m + \tfrac{1}{2}(\Delta E_{AV}^2 + \Delta E_{AV}^3), \tag{1}$$

where H_V^f and H_V^m are the formation and migration enthalpies of an isolated V, respectively, and ΔE_{AV}^i is the binding energy of the V at an ith nearest neighbor site from the impurity atom A. Equation (1) is therefore an approximation to the real barrier for motion of the V between the second and third nearest neighbor positions (see Fig. 2 in Ref. 39 and Table I).

The analysis by Dunham and Wu[39] contains a number of assumptions, the most significant being that H_V^m remains constant regardless of the relative position of the V and the dopant. To test this assumption, we implemented the linear synchronous transit (LST) method[40] to directly calculate the actual migration enthalpy barriers. The methodology and parameters used here were given in a recent study,[27] which predicted the migration of clusters in Ge. In contrast to the assumption of Dunham and Wu,[39] we predict that the migration enthalpy barriers are significantly affected by the presence of different dopant atoms in Ge (see Table I). Furthermore, as discussed by Höhler *et al.*,[41] oversized impurities in Ge prefer the split-V (or bond-centered) configuration, in which the impurity atom is surrounded by two semivacancies. Such configurations were not considered in the Dunham and Wu[39] analysis. To overcome these issues and to compare to the results of the Dunham and Wu[39] analysis, we also calculated Q_a by using the following definition:

$$Q_a = H_V^f + \Delta E_{AV}^1 + H_{AV}^m, \tag{2}$$

where H_{AV}^m is the greatest migration enthalpy barrier (calculated by using LST and reported in Table I) of a V along the ring and ΔE_{AV}^1 is the binding enthalpy of the AV pair at a full-V or split-V configuration (in the case of SnV), depending on which is more energetically favorable (see Table I). H_{AV}^m is the actual migration barrier of a V near a dopant atom (within the static lattice approximation), which is generally different to the bare migration barrier of an isolated V, as assumed by Dunham and Wu.[39] For example, Fig. 1 represents the differences in the AsV barriers between the Dunham and Wu[39] analysis and LST. The greatest migration enthalpy barrier predicted by the LST method is the exchange between the As atom and the V [i.e., in Fig. 1 the step from (5) to (6)] and not the progression of the V from the second to the third nearest neighbor positions [i.e., in Fig. 1 the step from (2) to (3)] assumed by Dunham and Wu.[39] Interestingly, it can be observed from Table I that for the acceptor atoms (Al, Ga, and In), most second and third nearest neighbor interactions are repulsive, whereas Si repels a V even at the first nearest neighbor site. For the acceptor atoms, this indicates that a V will bind with the dopant, but when it moves away, it will likely break free. Therefore, another V will then be required to transport the acceptor atom. This is again in contrast to the Dunham and Wu[39] analysis where it is assumed that V are bound to the dopant atoms at the second and third nearest neighbor sites.

Table II compares the predicted activation enthalpies of diffusion, using Eqs. (1) and (2) with previous experimental results. In this table, column 4 shows experimental data obtained from diffusion profiles analyzed by means of SIMS. Column 5 summarizes the activation enthalpies determined via earlier techniques. The reason for reviewing results from earlier techniques is because it is useful to appreciate the accuracy of these with respect to the latter SIMS studies especially in Ge where, for some impurities, recent SIMS results are not necessarily more accurate than earlier results determined via the other techniques. An example is Sn diffusion, where Friesel *et al.*[22] determined by means of SIMS a diffusion activation enthalpy of 3.26 eV. At about the same time, Kringhøj and Elliman[21] also used SIMS and determined an activation enthalpy of 3.05 eV, which is identical

TABLE I. Predicted binding (ΔE_{AV}^i, i=1, 2, 3) and migration enthalpies (H_{AV}^m) for impurity-vacancy clusters (in eV).

Defect complex	ΔE_{AV}^1	ΔE_{AV}^2	ΔE_{AV}^3	H_{AV}^m
AlV	−0.40	0.09	0.23	0.86
GaV	−0.15	0.11	0.20	0.69
InV	−0.96	−0.16	0.14	1.18
SiV	0.24	0.03	−0.01	0.53
SnV	−0.64	−0.14	0.05	1.50
PV	−0.52	−0.35	−0.26	1.10
AsV	−0.60	−0.31	−0.22	0.84
SbV	−0.70	−0.34	−0.18	0.71

TABLE II. Predicted activation enthalpies (eV) for impurity diffusion Q_a via a V-mediated mechanism compared to results from SIMS analyzes of impurity diffusion profiles and other techniques (A: incremental sheet resistance; B: p-n-junction; and C: radiotracer).

	Density functional theory		Experiment	
Defect complex	This study	Dunham and Wu analysis[a]	SIMS analysis	Earlier studies
AlV	2.86	3.26	3.45[b]	3.2[c] A
GaV	2.94	3.25	3.31[d]	3.0[e] B
InV	2.79	3.09	3.63[f]	2.78[g] C
SiV	3.17	3.11	3.32[h]	2.9[i]
SnV	3.26	3.05	3.26[l]; 3.05[j]	3.05[k] C
PV	2.98	2.80	2.85[m]	2.4[e] B
AsV	2.64	2.83	2.71[m]	2.9[n] B
SbV	2.41	2.84	2.55[m]	2.8[o] A

[a]Reference 39.
[b]Reference 7.
[c]Reference 6.
[d]Reference 8.
[e]Reference 23.
[f]Reference 11.
[g]Reference 10.
[h]Reference 15.
[i]Reference 12.
[j]Reference 21.
[k]Reference 20.
[l]Reference 22.
[m]Reference 2.
[n]Reference 24.
[o]Reference 25.

to the radiotracer result of Valenta.[20] Interestingly, the present DFT calculations predict values of 3.05 eV via the Dunham and Wu[39] analysis by using Eq. (1) but 3.26 eV by using Eq. (2).

From Table II, it is evident that, with the exception of In, the present predictions are in clear agreement with the experimental results. The case of In is more uncertain as the spread in experimental values is much greater. For example, the activation enthalpy for diffusion reported by Dorner *et al.*[11] is 3.63 eV, whereas the value determined by Pantaleev[10] is 2.78 eV. Indeed, early radiotracer and impedance measurements determined values for the In activation enthalpy in the range of 2.78–3.04 eV.[5,10] The present DFT calculations yield values of 2.79 [via Eq. (2)] and 3.09 eV [via Eq. (1)] and are thus in agreement with the earlier results from the radiotracer and impedance measurements but not with the data from the SIMS study of Dorner *et al.*[11] (i.e., 3.63 eV). It is possible, therefore, that Dorner *et al.*[11] overestimated the activation enthalpy of In diffusion.

In summary, by using two approaches, we have predicted the activation enthalpies of diffusion for eight important impurities in Ge. By calculating the barriers between the various states, we find that the approximations inherent in the approach of Dunham and Wu[39] [see Eq. (1)] and the values from Eq. (2) do not always agree, in particular, for the donor atoms (P, As, and Sb). Importantly, the Dunham and Wu[39] analysis fails to predict the underlying trend observed in the activation enthalpy of P, As, and Sb diffusion[2] that with increasing donor size Q_a decreases. Results derived by using Eq. (2) are consistent with this trend and as such demonstrate the importance of predicting migration energy barriers for each individual dopant. Nevertheless, the present experimental and theoretical data do not provide a clear picture for In diffusion in Ge. Direct comparison between the theoretical and experimental values determined for Q_a reveals a difference of 0.84 eV, which clearly exceeds the differences obtained for the other dopants. Experiments are currently underway to verify the activation enthalpy of In.

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