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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.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 experiments17 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.17 Previous experimental studies on Al diffusion yield activation enthalpies in the range of 3.2–3.45 eV.6,23 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 Pantaleev10 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.36,37 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

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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.12,78 Recent diffusion experiments15 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 Dunlap37 and Karstensen,23 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–Ernzerhof28 exchange-correlation functional in conjunction with ultrasoft pseudopotentials29 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–Pack32 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 B3LYP, 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...
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 \( E_B = E_{\text{defect-cluster}} - (E_{\text{isolated-defect}}) \)]. 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

\[
Q_a = H_V^i + H_V^o + \frac{1}{2}(\Delta E_{AV}^2 + \Delta E_{AV}^3),
\]

where \( H_V^i \) and \( H_V^o \) are the formation and migration enthalpies of an isolated \( V \), respectively, and \( \Delta E_{AV} \) is the binding energy of the \( V \) at an \( i \)th 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 \( H_V^o \) 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). Further-
to the radiotracer result of Valenta.20 Interestingly, the present DFT calculations predict values of 3.05 eV via the Dunham and Wu39 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 Panteleev10 is 2.78 eV. Indeed, early 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 Wu39 [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 Wu39 analysis fails to predict the underlying trend observed in the activation enthalpy of P, As, and Sb diffusion22 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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