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The vacancy in silicon: A critical evaluation of experimental and theoretical results

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Recent experimental studies of Shimizu *et al.* [Phys. Rev. Lett. **98**, 095901 (2007)] revealed an activation enthalpy of 3.6 eV for the vacancy contribution to Si self-diffusion. Although this value seems to be in accurate agreement with recent theoretical results, it is at variance with experiments on vacancy-mediated dopant diffusion in Si. In the present study we review results from electronic structure calculations and conclude that the calculations are consistent with an activation enthalpy of 4.5–4.6 eV rather than 3.6 eV for the vacancy contribution to self-diffusion. Moreover, our calculations predict activation enthalpies of 4.45 and 3.81 eV for the vacancy-mediated diffusion of phosphorus and antimony, respectively, in good agreement with the most recent experimental results. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2996284]

The technological application of silicon (Si) in electronic devices led to decades of research, and Si has become one of the most studied materials. In that respect it is surprising that the activation enthalpy of vacancy (V)-mediated self-diffusion is still controversial. Recent studies[1,2] support the view that the activation enthalpy of V-mediated self-diffusion is about 3.6 eV. This value, which comprises the sum of the V-formation and migration enthalpies, seems to be confirmed by recent theoretical results on the V-formation enthalpy of 3.17 eV and the energy barrier of 0.4 eV determined for vacancy hops.[3–5] However, the activation enthalpy of self-diffusion via vacancies becomes questionable by comparing with the activation enthalpy of dopant diffusion via vacancies. For example, antimony (Sb) is known to diffuse in Si via the vacancy mechanism with an activation enthalpy of 4.08 eV.[6] Also the activation enthalpy of 4.44 eV for the V-mediated contribution to phosphorus (P) diffusion in silicon clearly exceeds the activation enthalpy of 3.6 eV proposed for self-diffusion via vacancies.[7] Taking into account this value of 3.6 eV, the higher activation enthalpy of dopant diffusion implies a repulsive interaction between the substitutional Sb and the vacancy. As a consequence, it is less probable for an Sb atom to find a vacancy in the neighborhood compared to the probability of the vacancy in the undisturbed silicon lattice. Accordingly, it is to be expected that the diffusion coefficient of Sb is lower than that of Si. However, all experiments on Sb diffusion in Si clearly demonstrate that Sb diffusion is faster than self-diffusion, indicating an attractive rather than a repulsive interaction between Sb and the V.[6] Therefore, the activation enthalpy of Sb diffusion in Si represents a definitive lower bound for the activation enthalpy of self-diffusion via vacancies, that is, the activation enthalpy of V-mediated self-diffusion must be higher than 4 eV to be consistent with our understanding on V-mediated dopant diffusion in Si. In this respect, the value of 3.6 eV reported by Shimizu *et al.*[1] for self-diffusion via vacancies is at variance with the V-mediated dopant diffusion in Si.

At this point it is worthwhile to also review the situation of self- and dopant diffusion in Ge. In Ge, self-diffusion and the diffusion of the n-type dopants P, As, and Sb are fully mediated by vacancies.[8,9] The diffusion coefficients of the n-type dopants clearly exceed Ge self-diffusion, and the corresponding diffusion activation enthalpies are lower compared to the activation enthalpy of self-diffusion. In particular, the activation enthalpy of the n-type dopants decreases with the increasing size of the dopant, indicating an increasing binding energy of the dopant-vacancy complex.[9] Recent theoretical calculations of the activation enthalpy of P, As, and Sb diffusion in Ge not only reproduce the decreasing diffusion activation enthalpy with increasing size of the dopants but also agree quantitatively with the experimental results.[10] Uberuaga *et al.*[11] predicted an activation enthalpy of 3.1 eV for Ge self-diffusion that is in excellent agreement with the experimental result of 3.09 eV reported by Werner *et al.*[8] This agreement between experimental and theoretical results on the activation enthalpies of self- and dopant diffusion holds true for Ge and also for Si (see below) in the case an alternative functional, such as the B3YLP, is used in density functional theory (DFT) calculations, as discussed by Uberuaga *et al.*[11]

Previous DFT calculations[3–5] are known to underestimate the formation energies of defects in Si and Ge due to the lack of exact exchange in these functionals.[12–15] Although these are well converged studies employing supercells of up to 512 atoms and Brillouin-zone sampling with 2^3 k-points, the 3.17–3.29 eV values predicted for the V-formation enthalpy in Si[3,5] are a severe underestimation and are therefore not appropriate to facilitate comparison with the experimental studies that support 3.6 eV for self-diffusion via V in Si.[1,2] This issue was pointed out in numerous previous studies of group-IV semiconductors (see, for example, Refs. 16–18). By using advanced computational techniques such as quantum Monte Carlo or alternative

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exchange-correlation functionals (e.g., the B3YLP), this problem can be overcome.[14,16] These techniques predict, in the case of Si, formation enthalpies of defects that are about 1 eV higher than the normal DFT predictions.[14,16] For example, the B3YLP-corrected value of the activation enthalpy of self-diffusion via V in Si is 4.56 eV (3.98 eV for the formation and 0.58 eV for the migration enthalpy),[16] which is consistent with the activation of V-mediated dopant diffusion. This demonstrates that the activation enthalpy of 3.6 eV for V-mediated self-diffusion in Si proposed by Shimizu *et al.*[1] remains questionable.

Motivated by the accurate agreement between the experimental and theoretical results on V-mediated self- and dopant diffusion in Ge, we performed additional DFT calculations to predict the activation enthalpy of diffusion of phosphorus (P) and Sb in Si via the vacancy mechanism. For the prediction of the binding and migration enthalpies, which are less sensitive to the exchange-correlation functional (see, for example, Ref. 19), we used normal DFT techniques (see below), whereas for the V formation enthalpy we adopted the 3.98 eV value of Uberuaga.[16]

The calculations were performed with the CASTEP code.[20,21] For all the calculations, a 64-atom supercell Brillouin-zone sampling with a Monkhorst–Pack[22] grid of 2^3 k-points and a plane-wave basis set with a 350 eV energy cutoff were used. The generalized gradient approximation using the Perdew–Burke–Ernzerhof[23] exchange-correlation functional in conjunction with ultrasoft pseudopotentials[24] was applied. To predict the migration enthalpy barriers we implemented the linear synchronous transit method.[25] More details about the methodology and the adequate convergence of the computational parameters were demonstrated previously (Ref. 26 and references therein).

We calculated the activation enthalpy of diffusion of the AV pair Q_a via the ring mechanism of diffusion[27] using the following definition:

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

where H_{AV}^m is the greatest migration enthalpy barrier of a V along the ring (see inset of Fig. 1) and ΔE_{AV}^1 is the binding enthalpy of the AV pair at a full-V (in the case of PV) or split-V configuration (for Sb V, see Ref. 28 for description of configuration), depending on which is more energetically favorable.

Table I summarizes the binding and migration enthalpies for the P V and Sb V complexes. For Sb V the split-V configuration was predicted to be more bound by -0.8 eV (see Table I). This is in excellent agreement with the predictions of the DFT (within the local density approximation) study of Höhler *et al.*[28] that predicted an enthalpy difference from the full-V configuration of -0.68 eV. For P, the greatest migration enthalpy barrier predicted is the exchange between the P atom and the V [i.e., in Fig. 1 the step from (5) to (6)]. For Sb, the greatest migration enthalpy barrier is between the V at the third nearest neighbor with respect to Sb and the split-V configuration [i.e., in Fig. 1 the enthalpy barrier between configuration (3) and the step from (5) to (6)]. Taking into account the V-formation enthalpy of 3.98 eV obtained by Uberuaga,[16] activation enthalpies of 4.45 and 3.81 eV are obtained by means of Eq. (1) for P and Sb diffusion, respectively. These values are in good agreement with the experimental results of 4.44 ± 0.59 eV (4.08 ± 0.06 eV) for V-mediated P (Sb) diffusion in Si.[6,7]

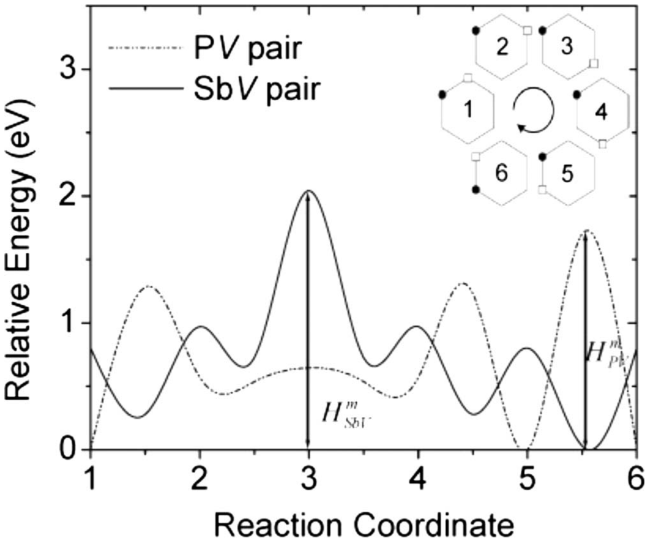

FIG. 1. The predicted migration enthalpy profile for the P V and Sb V pair in Si. The inset represents the ring mechanism of diffusion for the AV pair (donor atom=black circles and V=squares) projected onto the (111) surface of Si. H_{AV}^m is the migration barrier of a V near a dopant atom. In the case of P, H_{AV}^m is maximal for the site exchange between the dopant A and the V [see inset (step 5 to 6)]. For Sb, H_{AV}^m is maximal when the V moves to the third nearest neighbor site with respect to the dopant.

Additional experimental evidence of an activation enthalpy of V-mediated Si self-diffusion exceeding 4 eV stems from the comprehensive analysis of Si crystal growth, high temperature wafer processing, Si self-diffusion, and metal diffusion experiments performed by Voronkov and Falster.[29] These studies support an activation enthalpy of 4.33 eV for Si self-diffusion via vacancies. This value is consistent with the B3YLP-corrected value of 4.56 eV (see above)[16] and with our understanding on V-mediated dopant diffusion in Si. Taking into account the DFT calculations and the results of self-, dopant, and metal diffusion and analyses of crystal growth and high temperature wafer processing,[7,29] all these studies do not confirm the activation enthalpy of 3.6 eV for Si self-diffusion via V reported by Shimizu *et al.*[1]

The pre-exponential factor 9.6 $\mathrm{cm}^2\,\mathrm{s}^{-1}$ reported by Voronkov and Falster[29] for self-diffusion via vacancies suggests a diffusion activation entropy of about $9k_B$. This value comprises both the entropy of V-formation and migration. An entropy of about $9k_B$ also follows from the pre-exponential factor of self-diffusion in Ge (Ref. 8), which is known to be

TABLE I. Predicted binding (ΔE_{AV}^i, $i=1,2,3$) and migration enthalpies (H_{AV}^m) for impurity-vacancy pairs (in eV). ΔE_{AV}^i is the binding energy of the V at an ith nearest neighbor site from the impurity atom A. H_{AV}^m is the greatest migration enthalpy barrier of a V along the ring (see Fig. 1). The value in the brackets is for the split-vacancy configuration of Sb V.

Defect complex	ΔE_{AV}^1	ΔE_{AV}^2	ΔE_{AV}^3	H_{AV}^m
P V	−1.23	−0.66	−0.58	1.70
Sb V	−1.41(−2.21)	−1.24	−0.17	2.04

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mainly mediated by vacancies. In this respect, vacancies in Si and Ge behave very similarly. The pre-exponential factor of 0.0023 $\text{cm}^2\ \text{s}^{-1}$ reported by Shimizu *et al.*[1] for Si self-diffusion via vacancies yields an activation entropy of $0.5k_B$. Compared with Ge and against the background of the interrelation between the activation enthalpy of self- and dopant diffusion, this value is certainly too low. Reasons for the underestimation of the activation enthalpy and entropy of V-mediated self-diffusion could be related to the indirect approach to determine diffusion broadening of isotope superlattices by Raman measurements. In addition, grown-in defects may have affected the diffusion broadening, in particular at the lowest temperatures where transient diffusion effects can be more pronounced compared to thermal broadening, thereby suggesting a too low activation enthalpy and entropy of self-diffusion. The high values for the activation entropy of self-diffusion in Si and also in Ge led Seeger and Chik[30] many years ago to propose their concept of extended native point defects to explain differences between the low and high temperature properties of monovacancies. Although this concept has not yet been verified, it is also not disproved by the experiments of Shimizu *et al.*[1]

In conclusion, the good agreement between the activation enthalpy of 3.6 eV for the vacancy contribution to Si self-diffusion[1] and the recent theoretical results[3] is misleading since the considered theoretical studies underestimate the formation enthalpy of V in Si. In the case when the more appropriate B3YLP functional is used for the computational calculations, the theory predicts a diffusion activation enthalpy of 4.56 eV for Si self-diffusion via vacancies. This value is fully consistent with the results on V-mediated diffusion of P and Sb in Si[6,7] and the properties of vacancies deduced from crystal growth and thermal processing of Si wafers.[29] The interrelation between self- and dopant diffusion discussed in this work does not question the low barrier for vacancy diffusion in Si determined many years ago by Watkins and co-wrokers.[2,31,32] However, the concept of extended native point defects that was questioned in a recent paper by Watkins[2] is definitely *not* disproved by the experiments of Shimizu *et al.*[1]

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