Microscopic Theory of Impurity-Defect Reactions and Impurity Diffusion in Silicon

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We present the first microscopic calculations of the energetics of impurity-defect reactions and provide a detailed picture of the diffusion mechanisms of dopant impurities in Si. We find that vacancies mediate impurity diffusion via impurity-vacancy pairs. Self-interstitials mediate diffusion by ejecting substitutional impurities into interstitial channels and/or via impurity–self-interstitial pairs. The predicted activation energies for P and Al agree well with measured values in both intrinsic and extrinsic Si.

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Impurity diffusion constitutes a fundamental solid-state phenomenon which plays a central role in the fabrication of electronic devices. Modeling of diffusion profiles, which lies at the heart of device design, depends on the underlying diffusion mechanisms. In Si, the premier device material, the essential aspects of these mechanisms have not been established, because microscopic calculations have been lacking altogether and available data can be fitted or interpreted with different sets of assumptions.[1] Device design is currently based on complex computer programs which grew over years of empirical experience and skillful insight.

In this paper, we describe the first microscopic calculations of the energetics of reactions between dopant impurities and intrinsic defects in Si. We report results for reactions which underlie several diffusion mechanisms and predict activation energies which agree well with measured values. In addition, our results lead to detailed descriptions of the diffusing species, their atomic configurations, charge states, and paths. We find that vacancies mediate diffusion via impurity-vacancy pairs, but "interstitialcies" are not necessarily the primary mechanism of self-interstitial contributions, as previously[1] assumed. Instead, we find that self-interstitials may also contribute via the "kick-out" mechanism (i.e., ejection of substitutional impurities into interstitial channels), which had so far been deemed active only in the case of heavy atoms such as gold.

Let us first set out some general principles which govern the diffusion of atoms at normal atomic sites, whether they are "marked" Si atoms (self-diffusion) or substitutional impurities. Such diffusion is mediated by defects in the following sense: Defects migrate randomly, and occasionally induce a marked atom to move to a different site. Under equilibrium conditions, the net activation energy is always the sum of the diffusing defect's formation and migration energy. In the case of self-diffusion, the diffusing species is an intrinsic defect (vacancy, self-interstitial, etc.). Substitutional impurities can diffuse in principle by the same mechanisms, i.e., the diffusing species are the same intrinsic defects. The impurity activation energies are then the same as for self-diffusion.[2] In contrast, the experimental activation energies of dopant impurities in Si are typically ~ 1 eV smaller than the self-diffusion activation energy.[3] It is clear that more complex mechanisms are active, i.e., the diffusing species are defects which are products of reactions between intrinsic defects and substitutional impurities. The activation energy (sum of formation and migration energies of the diffusing species) can then be smaller than the self-diffusion activation energy. Our main objective here is to identify and describe the impurity-defect reactions that are responsible for the observed reduction in activation energy. We chose phosphorus as a representative donor impurity and aluminum as a representative acceptor impurity. All calculations have been carried out by use of the Green's-function method as reported elsewhere[4]; we reported activation energies for vacancies and self-interstitials and gave a detailed description of self-diffusion. The results of Ref. 4 have been corroborated by independent calculations.[5] Technical details of our method and our calculations will be published elsewhere. We estimate our theoretical error bar to be of order 0.5 eV.

Let us first consider vacancies (V), which contribute to self-diffusion with activation energies[4,6] in the range of observed values (Table I). The only possible reaction between a thermally created vacancy and a substitutional impurity is the formation of a pair. It has indeed been recognized that substitutional impurities may diffuse by a mechanism where the diffusing species is an impurity-vacancy pair.[1,7,8] In Figs. 1(a) and 1(b), we show the calculated formation energy of P-V and Al-V pairs for different charge states as a function of the Fermi-level position in the energy gap. Combining this figure with the corresponding figure for the vacancy formation energy,[4,6] one can extract binding energies for the various charge states of the pair and various initial charge states of the constituent defects. For example, the neutral P-V pair formed from neutral constituents has a binding energy of 1.8

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TABLE I. Theoretical and experimental activation energies (in electronvolts) for self-diffusion (SD) in intrinsic Si, P diffusion in intrinsic and n-type Si, and Al diffusion in intrinsic and p-type Si.

Species	$Q_{\rm int}$	Species	$Q_{\rm int}$	Q_n	Species	$Q_{\rm int}$	Q_p
			Theory				
V^{++}	5.1	$(P_s V)^+$	3.2	3.8	$(Al_s V)^+$	3.9	3.2
V^+	4.7	$(P_s V)^0$	3.0	3.0	$(Al_s V)^0$	3.5	3.5
V^0	4.2	$(P_s V)^-$	3.2	2.6	$(Al_s V)^-$	3.5	4.1
V^-	4.5	$(P_s I)^0$	5.7	5.7	$(Al_s I)^0$	4.0	4.0
I^{++}	5.6	$(P_i)^0$	5.1	5.1	$(Al_i)^{++}$	4.3	3.0
I^+	5.5	$(P_i)^-$	5.2	4.6	$(Al_i)^+$	3.9	3.1
I^0	5.7	$(P_i)^{--}$	5.6	4.5	$(Al_i)^0$	3.9	3.9
			Experiment				
SD	4.1–5.1[a]	P	3.7[b]	3.1[b]	Al	3.5[c]	. . .

[a]See compilation of experimental values in Ref. 9.
[b]J. S. Makris and B. J. Masters, J. Electrochem. Soc. **120**, 1252 (1973).
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eV. Figures 1(a) and 1(b) also reveal that the $-/0$ energy level of P-V is at about $E_c - 0.4$ eV and the $0/+$ level of Al-V is at about $E_v + 0.4$ eV, both in very good agreement with experimental values.[7,8]

The migration path for the impurity-vacancy pair was described in 1964 by Watkins and Corbett[7]: The vacancy moves around a sixfold ring and places itself in front of the impurity, the impurity jumps into the vacant site, and the vacancy again moves around a sixfold ring to go in front of the vacancy. Computer capacity does not allow us to calculate this migration energy. We, therefore, use the value measured by Watkins and Corbett[7] (~ 1 eV) for the neutral P-V pair and estimate its charge-state dependence to be negligible. We arrive at the activation energies listed in Table I. Annealing studies[7] suggest a similar migration energy for the Al-V pair, resulting in the activation energies listed in Table I. We will discuss these results after we present results for self-interstitial–mediated diffusion.

We now turn to the role of self-interstitials (I), which also mediate self-diffusion.[4] Because of the lack of reliable information abut the energetically favorable configurations of the Si self-interstitial, detailed models for the role of self-interstitials in mediating impurity diffusion have not been advanced. Most authors assume that the diffusing species is an "interstitialcy,"[1] i.e., an impurity atom and a Si atom sharing an atomic site. Such a defect is an example of an impurity–self-interstitial pair, analogous to the impurity-vacancy pair discussed above, but its structure and motional mechanism have not been established.

In addition to pair formation, however, self-interstitials can induce the "kick-out" reaction: a self-interstitial can take the place of a substitutional impurity by kicking it into an interstitial site, from where it can migrate through the lattice until the reverse reaction occurs. In this mechanism, which has been invoked for Au in Si,[9] but not for shallow dopants, the diffusing species is the interstitial impurity atom.

We have investigated several configurations involving an impurity atom and N Si atoms vying for N atomic sites: simple impurity–self-interstitial pairs consisting of a substitutional impurity and a Si atom at a nearby tetrahedral (T) or hexagonal (H) intersitial site; "interstitialcies" consisting of an impurity atom and N Si atoms sharing N atomic sites [e.g., the self-interstitial may be at the bond-center (B) site next to the impurity, which is displaced in the opposite direction, or vice versa]; and interstitial impurities at channel sites (e.g., T or H) no longer bound to any of the N Si atoms occupying the N atomic sites.

The formation energy of each configuration depends on the charge state and the position of the Fermi level. Selected results are shown in Figs. 1(c)–1(f). We see that, in contrast to the self-interstitial,[4] P and Al are not negative-U systems. We also see that, for the relevant Fermi-level positions, the lowest-energy configuration is the one with the impurity in the channel (T site for Al, H site for P) where the migration barrier is rather small (~ 1 eV). The net diffusion activation energies are given in Table I.

The present calculations do not allow us to determine whether impurity–self-interstitial pairs are completely unstable or metastable, higher-energy diffusing species. For other impurities, they may even be the stable species. We have, therefore, examined possible motional mechanisms and use Fig. 2 to illustrate one of them: The self-interstitial initially occupies a T site next to the impurity. It then replaces the impurity by pushing it in the (111) direction to the next atomic site

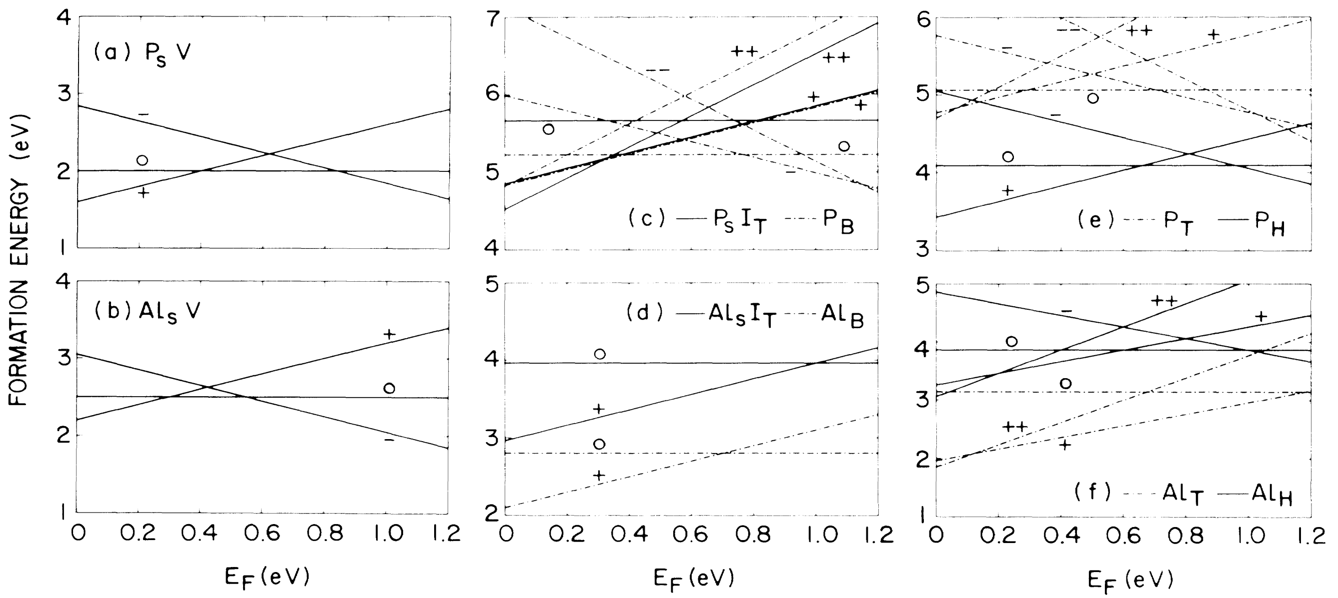

FIG. 1. Formation energies of several defects described in the text. The subscript s denotes substitutional, the others denote interstitial sites as in the text. E_F is the position of the Fermi level relative to the top of the valence bands.

while the impurity is ejecting the Si atom occupying that site into the channel on the other side [Fig. 2(a)]. The new Si interstitial swings around and places itself at the T site behind the impurity [Fig. 2(b)], from where it pushes through again [Fig. 2(c)], and so on. Note that through the path, the configuration changes from a simple pair (substitutional impurity, self-interstitial at a T site) to an "interstitialcy" (the impurity atom at the bond center), etc. In Table I we list the activation energy for this process for Al and P.

As Table I reveals, all the mechanisms that we considered above lead to a reduction in the impurity activation energy from the corresponding self-diffusion activation energy, as observed experimentally.[3] The relative importance of each mechanism, however, depends also on the formation and migration entropies of the diffusing species, which are not known. Experiment measures an effective activation energy which is, in general, near the lowest individual activation energy. The entries of Table I reveal a satisfactory agreement between theory and experiment for intrinsic Si. Furthermore, we reproduce the observed lowering of the P activation energy in extrinsic Si and conclude that it arises from the emergence of negatively charged species in n-type Si (cf. Fig. 1). We predict a similar enhancement for Al in heavily-doped p-type Si.

The results we presented above are also in agreement with a variety of other observations: Our prediction that it is energetically favorable for self-interstitials to kick substitutional Al's into the T site was previously deduced from low-temperature irradiation experiments by Watkins.[10] Our prediction that P diffusion is mediated by both vacancies and self-interstitials is consistent with conclusions based on the modeling of experimental data,[1] but no definite conclusion can be reached by either theory or experiment about the relative importance of each mechanism.

In summary, we have presented a detailed picture of several complex mechanisms of dopant impurity diffusion in Si. Our results differ in significant ways from the assumptions normally made in modeling diffusion data.[1] In particular, as in the case of self-interstitials whose migration in the channels was only recently recognized,[4,11] we now find that channel migration of dopant impurities plays a role in impurity diffusion. The new theoretical results should now form the basis for a reassessment of the modeling of diffusion data.

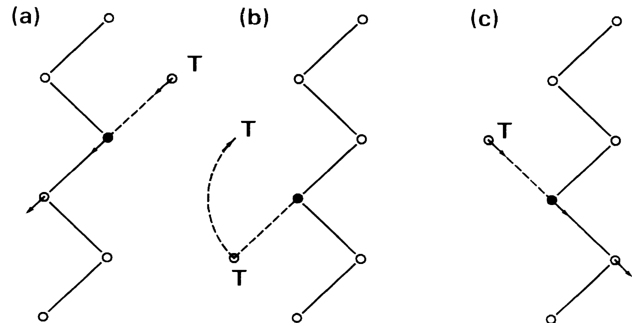

FIG. 2. Three stages in the migration of a pair consisting of a substitutional impurity (solid circle) and a self-interstitial in Si. The chain of Si atoms lies in the (110) plane.

They can also form the basis for an interpretation of an assortment of enhanced diffusion processes, such as oxidation-enhanced diffusion, rapid thermal annealing, rapid quenching, etc.

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