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THEORETICAL DETERMINATION OF THE VACANCY MIGRATION ENERGY IN SILICON

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Abstract

We have calculated the migration energy, E_M, for two charge-states of the isolated silicon lattice vacancy using a self-consistent Green's function technique within the local density approximation. These activation energies have been determined experimentally to be 0.45 eV for the neutral vacancy, V^0, and 0.33 eV for the doubly positively charged vacancy, V^{2+}. The values calculated assuming a simple migration path, which nevertheless involves substantial lattice relaxation, are 0.27 and 0.42 eV respectively.

Introduction

Because of the success achieved in calculating ground state properties of solids using the local density approximation [1], it is believed that if one could apply it with sufficient accuracy to calculations for point defects it would be possible to predict the energetics of those defects. These are, more often than not, inaccessible to experiment but are very important for obtaining a detailed understanding of the phenomena associated with the defects. Several calculations of defect energies have recently demonstrated the usefulness of such calculations in applications to self-diffusion [2,3] and impurity diffusion [4] in silicon, the calculation of the relative concentrations of native defects in GaAs [5], and defect identification in silicon [6]. In those cases where the calculations can be compared with one another [2,3], the agreement is reasonable. However, a direct comparison with experiment would be highly desirable. In most of the cases mentioned, such a comparison is not possible. Part of the reason is that it is frequently difficult to identify an experimental activation energy with a particular defect. A good example of this is self-diffusion in silicon [7]. At high temperatures the activation energy is determined to be between 4.1 and 5.1 eV. The difficulty arises in splitting this activation energy into a formation energy, E_F, and a migration energy, E_M, and identifying the associated defect. An additional complication is that the calculations are carried out for zero temperature and constant volume, whereas most experiments are performed at constant pressure and often high temperatures are required

to obtain a sufficiently high concentration of defects. The importance of correcting for these effects in silicon is not known.

The aim of this contribution is to calculate an activation energy which we can compare with experiment in a case where the defect involved has been unambiguously identified and temperature effects are negligible.

The defect we choose to study is one of the most studied defects in silicon, namely, the isolated silicon lattice vacancy. While the most recent experimental determination of the formation energy of the vacancy [8] agrees quite well with the latest theoretical values [2,3], the problem still remains of comparing calculations for zero temperature with experiments performed at temperatures close to the melting point. We therefore focus on the migration energy of the vacancy which has been measured with high precision by Watkins [9,10] for three different charge-states. It was possible to perform these experiments at low temperatures (140 - 180 K) by forming the vacancies by irradiation.

Method of Calculation

The method we use to calculate the total energy within the local density approximation is the Green's matrix method [11] which we have used previously to calculate the vacancy formation energy and the formation and migration energies of self-interstitials in silicon [2,4]. In our implementation we use norm-conserving pseudopotentials [12] and Gaussian orbitals and include long-range relaxation using a Keating model [13]. Full details will be given in a forthcoming publication [14].

In order to calculate the vacancy migration energy we need to know its stable configuration and the migration path. A fairly complete model of the low-temperature silicon vacancy now exists. Based on his early ESR studies on silicon irradiated at low temperature, Watkins gave a very simple description of the electronic structure of the vacancy, in terms of the molecular orbitals formed by the four dangling bonds of the atoms surrounding the vacancy [10]. For the undistorted vacancy these four dangling bonds give rise to a singly degenerate level which forms a resonance in the valence band and a threefold degenerate state in the fundamental gap. Watkins interpreted his ESR data on the basis of the symmetry-lowering distortions induced by partially occupying the degenerate state. His model for the electronic structure was confirmed by self-consistent Green's function calculations [15,16]. Baraff, Kane and Schluter [17] constructed a simple model for the total energy of the vacancy, which included lattice distortion, and used their first principles calculations to evaluate some of the parameters of this model. This was sufficient to enable them to propose that the silicon vacancy formed a negative U system, which was soon confirmed experimentally [18].

This is also the geometry which we have assumed is the most stable configuration and we have used it to calculate the formation energy of several charge-states of the vacancy. We use the undistorted site symmetry, T_d , to label this configuration. We make the simplest possible choice for the migration path, namely, that a neighbouring lattice atom hops along a bond and displaces the vacancy. The saddle point which we examine is the configuration with an atom at the mid-bond site. Without distortion this geometry has D_{3d} symmetry and we label this configuration accordingly.

In all of our calculations of activation energies we make the static approximation i.e. we assume that the total energy of a particular configuration is obtained by allowing all neighbouring atoms to relax fully. While this is reasonable for the stable con-

figuration, it is not obviously so for the saddle point. This problem can only be studied by comparing the results of molecular dynamics and molecular statics calculations. In the limited number of cases where this has been done, it appears that the static approximation does not result in serious error [19].

Results and Discussion

Our results are summarized in Table 1 for two charge-states of the vacancy. We calculate the migration energy of the doubly positively charged vacancy to be 0.98 eV without, and 0.42 eV with, relaxation. For the neutral vacancy the corresponding numbers are 0.52 and 0.27 eV respectively.

Table 1 Formation energies of the silicon vacancy at the stable T_d site and at the assumed D_{3d} saddle point. For the doubly charged vacancy, we assume that the Fermi level is pinned at the top of the valence band. All energies are in electronvolts.

		E_F		E_M
		T_d	D_{3d}	
V^{2+}	Unrelaxed	3.43	4.41	0.98
	Relaxed	3.43	3.85	0.42
	Experiment			0.33
V^0	Unrelaxed	4.49	5.01	0.52
	Relaxed	3.92	4.19	0.27
	Experiment			0.45
V^{2-}	Experiment			0.18

We begin our discussion of these results with the V^{2+} . This is simpler than the V^0 because the electronic structure is non-degenerate at the T_d site and we need only consider symmetric modes of relaxation of the neighbouring atoms. We find that, without relaxation, the V^{2+} has a formation energy of 3.43 eV at the T_d site, assuming that the Fermi level is fixed at the top of the valence band. In p-type material the position of the Fermi level is determined by the position of the acceptor level, $\varepsilon_a \simeq 0.02 - 0.07$ eV, depending on the dopant species. Taking this into account makes a correction to the formation energy of the order of $2\varepsilon_a$, but does not affect the migration energy for a particular charge-state. The magnitude of the symmetric breathing relaxation of the neighbouring four atoms is < 0.01Å so that the formation energy is essentially unchanged. At the D_{3d} site, the formation energy without relaxation is 4.41 eV. There are two states in the gap, a singly degenerate a_1 level which lies above a doubly degenerate e level. Both of these states are unoccupied so that, as before, we need only consider a symmetry-conserving breathing relaxation. Including long-range relaxation, we find that there is a large inward relaxation where each of the six nearest neighbour atoms of the migrating atom is displaced towards it ('inwards') by 0.26Å and there is a total energy gain of 0.56 eV. The resulting migration barrier is thus 0.42 eV compared to the experimental value of 0.33 eV.

The case of the neutral vacancy is more complicated because symmetry-lowering distortions occur for both T_d and D_{3d} configurations. The unrelaxed formation ener-

gies are 4.49 and 5.01 eV respectively. At the T_d site there is a triply degenerate t_2 state in the gap which is doubly occupied. The calculated displacement of each of the 4 neighbour atoms in the resulting $T_d \rightarrow D_{2d}$ distortion [10] is 0.28Å , with a net reduction of the formation energy of 0.44 eV. We calculate an inward (towards the vacancy) breathing, with each of the four neighbouring atoms being displaced by 0.20Å and an energy gain of 0.13 eV. The final V^0 formation energy is thus 3.92 eV [2]. For the D_{3d} configuration, we calculate a large inward breathing of the six nearest neighbour atoms of 0.28Å which reduces the formation energy by 0.79 eV. The lowest lying state in the gap is doubly degenerate and only half-occupied so that we expect a symmetry lowering distortion. We have considered two such possible distortions. In one of these, the migrating silicon atom is displaced in the mirror plane perpendicular to the bond direction ($D_{3d} \rightarrow C_{1h}$) . The calculated gain in energy is less than 0.01 eV. In the other distortion which we have considered, the threefold rotation symmetry is broken by four of the six nearest neighbour atoms pairing ($D_{3d} \rightarrow C_{2h}$) . The gain in energy is only 0.03 eV so that the resulting formation energy is 4.19 eV. The migration energy is therefore 0.27 eV compared with the experimental value of 0.45 eV. Our calculations result in migration energies for the silicon vacancy which are in much better agreement with experiment than previous estimates [20]. They are significant because they represent the first comparison of such total-energy calculations with activation energies measured at low temperature and give an indication of the accuracy of the approximations we have made.

Calculations have only been reported for the electronic structure of the T_d configuration vacancy and, where comparison is possible, we find reasonable agreement - except on one point, the direction of the breathing relaxation of the four nearest neighbours. In the most detailed theoretical study of the vacancy so far, Baraff, Kane and Schluter [17] assumed an outward breathing of the neutral vacancy of 0.10Å , by analogy with the silicon (111) surface. From their calculation of the deformation potential they then arrived at a value of 0.23Å for the outward breathing of the V^{2+} . In their subsequent comparison of derived calculated quantities with experiment, they concluded that the assumed magnitude of the outward breathing was too large, but that a more precise determination was not justified by the accuracy of the calculation. There have been two other direct calculations of the breathing relaxation of the vacancy by Lindefelt [21], and by Scheffler et al. [22], who also used self-consistent Green's function methods and calculated the force on the atoms surrounding the vacancy using the Hellmann-Feynman theorem. Both these calculations found an outward breathing relaxation. Scheffler et al. found the same charge-state dependence of the breathing as Baraff et al. and as, indeed, we do. We can therefore restrict our attention to the simpler issue of whether the V^{2+} breathes inwards or outwards. The mechanism usually invoked to explain the relaxation of the unreconstructed Si(111) surface-atoms towards the bulk atoms is their tendency to form graphite-like sp^2 bonds which are all occupied rather than three occupied and one unoccupied sp^3 bond. The energy gained by this relaxation is calculated to be about 0.15 eV per surface atom [23] or 0.6 eV for the vacancy with four 'surface' atoms. In the case of the vacancy the situation is complicated by the overlap of the dangling bonds which give rise to the triply degenerate anti-bonding t_2 state and the singly degenerate bonding a_1 state. In the case of the V^{2+} only the bonding level is occupied and the $a_1 - t_2$ splitting, which is calculated to be about 0.8 eV, is a measure of the strength of the bond formed. This bond tends to cause the vacancy to relax inwards and the final result depends on a cancellation of these two effects. Since the discrepancy of our calculated migration energies with experiment is comparable to the energy gained by breathing, we conclude that we cannot, at present, resolve this issue. Here, we merely make two closing remarks about the direction of the breathing in our calculation.

The first is that a smaller inward breathing of the neutral vacancy or a small outward relaxation would lead to a larger formation energy for V^0 and hence a smaller theoretical migration energy which is already slightly too small. Similarly, the formation energy for the V^{2+} would be decreased somewhat and thus the theoretical migration energy, which is already slightly too large, would be increased.

The second point is that, within our computational accuracy, we still find negative-U behaviour for the vacancy, as required by experiment. We therefore conclude that there is at present no compelling experimental evidence in favour of an outward relaxation.

Conclusions

As a test of the accuracy of total-energy differences for point defects achievable with our Green's function programme, we have calculated the migration energy for two charge-states of the silicon lattice vacancy. With a static approximation and assuming the simplest migration path, we find sufficiently good agreement with experiment to conclude that we can calculate changes in energy of the order of 0.1 eV.

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