Electronic structure of complex defects in silicon: divacancy and split 100 interstitial

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Résumé. — On a utilisé la méthode des fonctions de Green et une description en liaisons fortes de la structure de bande du silicium pour traiter la structure électronique de défauts complexes: la bilacune et l'intersticiel dissocié 100. Les résultats sont comparés avec ceux obtenus à l'aide de la méthode de Hückel étendue. On en tire quelques conclusions sur la meilleure utilisation de la présente méthode.

Abstract. — The Green’s function method together with a tight binding parametrisation of the band structure on Si are used to calculate the electronic structure of complex defects: the divacancy and the split 100 interstitial. Results are compared with E.H.T. calculations and some general conclusions on the best use of the method are drawn.

1. Introduction. — Recently, two self consistent calculations of the electronic structure of the silicon vacancy have been performed within the Green’s function formalism [1]. This procedure avoids any use of cluster approximations, which appear to be unsatisfactory for this problem [2].

Previous calculations with the Green’s function method which used a second neighbour interactions tight binding model of the band structure of silicon [3] are in semi quantitative agreement with these more recent works. The phase shifts in the valence band are quite similar, the $T_2$ bound state in the gap being somewhat too low in the tight binding calculation.

The main advantage of the tight binding method is to be computationally much simpler so that it can be easily extended to treat more complicated defects. The main purpose of this work is to test the efficiency of this procedure for such defects, to see what are the new problems which arise then, and to determine in which conditions the method can be best used in this context.

As test cases, we have treated the divacancy (unrelaxed and relaxed), and the split 100 interstitial configuration. The calculational procedure has been presented before [3] and we shall only recall that to obtain the Green’s functions we use the continuous fraction expansion of Haydock et al. [4].

2. Divacancy. — 2.1 Unrelaxed Divacancy. — The group symmetry of the unrelaxed divacancy is $D_{3d}$. In this group, the s and p orbitals on two neighbouring sites give rise to the following irreducible representations:

$$2 \times A_{1g} + 2 \times A_{2u} + E_g + E_u.$$

The corresponding symmetry orbitals are given in table I.

Table I. — Symmetry orbitals for the divacancy.

<table>
<thead>
<tr>
<th>$A_{1g}$</th>
<th>$A_{2u}$</th>
<th>$E_g$</th>
<th>$E_u$</th>
<th>$A_1$ (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_x$</td>
<td>$A_y$</td>
<td>$B_x$</td>
<td>$B_y$</td>
<td>$A_z$</td>
</tr>
<tr>
<td>$[1x]$</td>
<td>$[1y]$</td>
<td>$[1z]$</td>
<td>$[2x]$</td>
<td>$[2y]$</td>
</tr>
<tr>
<td>$a$</td>
<td>$b$</td>
<td>$b$</td>
<td>$b$</td>
<td>$a$</td>
</tr>
<tr>
<td>$b$</td>
<td>$c$</td>
<td>$d$</td>
<td>$c$</td>
<td>$b$</td>
</tr>
<tr>
<td>$b$</td>
<td>$c$</td>
<td>$d$</td>
<td>$d$</td>
<td>$b$</td>
</tr>
<tr>
<td>$a$</td>
<td>$b$</td>
<td>$b$</td>
<td>$b$</td>
<td>$a$</td>
</tr>
</tbody>
</table>

$A = \frac{1}{2}, \quad b = \frac{1}{\sqrt{6}}, \quad c = \frac{1}{2}, \quad d = \frac{1}{\sqrt{12}}$

(*): Unrelaxed.

(**): Relaxed.

To find the electronic levels associated with the divacancy, we start from one of the symmetry orbitals $|\Gamma i\rangle$ and generate the first vector of Haydock algorithm:

$$|\Gamma' i\rangle = H |\Gamma i\rangle - a_1 |\Gamma i\rangle$$
$|\Gamma' i\rangle$ is a linear combination of orbitals on the first and second neighbours of the two starting atoms, of the same symmetry as $|\Gamma i\rangle$. These two atoms are then withdrawn to create the divacancy and diagonal elements $\langle \Gamma' i | G | \Gamma' i \rangle$ are calculated. The electronic levels associated with the divacancy are clearly seen in the imaginary part of these Green’s function. The same procedure can be applied when relaxation of the atoms have been introduced since the Haydock algorithm does not use the periodicity of the lattice. Only a few Green’s function are the needed compared to the large number which would be necessary with the traditional way of computing Green’s function, where the starting point has to be the perfect crystal.

The results for the unrelaxed vacancy are given in table II, for two tight binding fits of the silicon band structure. A striking feature is that the bound states $E_u$ and $E_g$ are close to the monovacancy $T_2$ levels (0.12 eV and 0.20 eV in the two models). We believe that this is due to the lack of third and fifth neighbour interactions in the tight binding Hamiltonian. In Lee and McGill [5] E.H.T. calculation, where such interactions are present, the $E_u-E_g$ separation is much larger. The same procedure can be applied when relaxation of the atoms have been introduced since the Haydock algorithm does not use the periodicity of the lattice. Only a few Green’s function are the needed compared to the large number which would be necessary with the traditional way of computing Green’s function, where the starting point has to be the perfect crystal.

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### Table II. — Electronic levels of the unrelaxed divacancy:

<table>
<thead>
<tr>
<th></th>
<th>$A_{1g}$</th>
<th>$A_{2u}$</th>
<th>$E_u$</th>
<th>$E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>-0.91</td>
<td>-0.58</td>
<td>0.12</td>
<td>0.15</td>
</tr>
<tr>
<td>b)</td>
<td>-0.94</td>
<td>-0.63</td>
<td>0.20</td>
<td>0.23</td>
</tr>
</tbody>
</table>

For the neutral divacancy, two electrons sit in $E_u$, as shown by phase shifts study [12]. In Lee and McGill [5], this level lies in the valence band. This can be due to vacancy-vacancy interactions, since they used periodic boundary conditions and consequently has a high divacancy concentration.

2.2 RELAXED DIVACANCY. — We have treated the same relaxation as Lee and McGill [5], which was suggested by Watkins and Corbett [6]. This relaxation is shown in figure 1. The divacancy is in d and d’, the pair of atoms a and c (a’ and c’) moves toward each other, while the atoms b and b’ move away from each other. With the distortion parameters $\alpha$ and $\beta$, the position of the atoms is the following [5] :

- $a = a_0 \left\{ \begin{array}{l} (1-\beta) e_x -(3-\beta) e_y -(3+\alpha) e_z \end{array} \right\}/8$
- $a' = a_0 \left\{ \begin{array}{l} -(1-\beta) e_x +(3-\beta) e_y +(3+\alpha) e_z \end{array} \right\}/8$
- $b = a_0 \left\{ \begin{array}{l} -(3+\beta) e_x -(3+\beta) e_y +(1+\alpha) e_z \end{array} \right\}/8$
- $b' = a_0 \left\{ \begin{array}{l} (3+\beta) e_x +(3+\beta) e_y -(1+\alpha) e_z \end{array} \right\}/8$
- $c = a_0 \left\{ \begin{array}{l} -(3-\beta) e_x +(1-\beta) e_y -(3+\alpha) e_z \end{array} \right\}/8$
- $c' = a_0 \left\{ \begin{array}{l} (3-\beta) e_x -(1-\beta) e_y +(3+\alpha) e_z \end{array} \right\}/8$

where $a_0$ is the lattice parameter and

$$\beta = \frac{(4 \alpha - \alpha^2)^{1/2}}{2}.$$
McGill [5] and different from that proposed by Watkins and Corbett [6]. It was suggested by Messmer [8] that this was due to vacancy-vacancy interactions in Lee and McGill [5] calculation. As our calculation is free of such interactions, this suggestion does not appear to be correct.

In the present state of the calculation, the comparison with experiment is difficult. However, the group of transitions at 0.35 eV (Chen and Corelli [9]) could be related with the allowed transition \( A_u \to B_g \) with a dipole moment \( xy \) (Fig. 2).

3. Split 100 interstitial. — The electronic structure of the tetrahedral and hexagonal interstitials have been calculated in [3] using the present method. The split 100 interstitial (Fig. 3) initially proposed by Friedel, has been used by Frank [10] for the interpretation of internal friction experiments.

We have investigated three possible configurations for this interstitial. In the first, atoms 1 and 2 are separated by the first neighbour distance in the perfect crystal. In the last, the distance between atom 1 and atoms 2, 3 and 4 are equal. The second is intermediate between these two extrem cases. No relaxation of the first neighbours has been introduced. The matrix elements of the Hamiltonian are calculated as in 2.2: The tight binding model used for the perfect crystal is that of Kauffe et al. [3].

The density of states for an interstitial site are shown in figure 3. Three levels appear in the gap for configuration 1 and 2. One can note the low localisation of the bound states as in the E.H.T. calculation of Weigel et al. for diamond [11]. The localisation on the first neighbours (Fig. 4) is also very weak.

For configuration 3, there are only two bound states in the gap. This is the only interstitial configuration among those considered by the present method (including the bond center interstitial [12]) which could correspond to the two levels scheme of Frank [10].

Fig. 3. — Split 100 interstitial.

Fig. 4. — Density of states on one of the atoms of the split 100 interstitial, for each of the three configurations described in the text. The heights of the bound states are proportional to their localisation on the site.

Fig. 5. — Density of states on a first neighbour of the interstitial for the three configurations described in the text.
4. **Conclusion.** — As shown in 2 and 3, the present method can be used as a practical tool to investigate complex defects without cluster approximations. It is also clear that some improvement are needed to allow a better comparison with experiments. Inclusion of third neighbour interactions (at least $pore$) will split the $E_u$ and $E_g$ level of the divacancy and rise both of them in the gap, since it will rise the $T_2$ level of the monovacancy (by widening the conduction band). Some further study of the variation of the Hamiltonian matrix elements with the distance is also necessary. It seems that the method should be most useful as an extrapolation method. The parameters ought to be determined so as to reproduce the results of more fundamental study of the relaxed monovacancy in silicon [13]. It could then be used to study other configurations of the monovacancy or more complex defects. A similar path, as been followed by Pandey and Phillips [7] in the surface problem, starting from the *first principles* calculation of Appelbaum and Hamann [14].

**References**


