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Electronic structure of divacancy–hydrogen complexes in silicon

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Abstract
Divacancy–hydrogen complexes (V_2H and V_2H_2) in Si are studied by *ab initio* modelling using large supercells. Here we pay special attention to their electronic structure, showing that these defects produce deep carrier traps. Calculated electrical gap levels indicate that V_2H_2 is an acceptor, whereas V_2H is amphoteric, with levels close to those of the well known divacancy. Finally our results are compared with the available data from deep level transient spectroscopy and electron paramagnetic resonance experiments.

1. Introduction

Vacancy-like defects in silicon are known to produce deep carrier traps within the forbidden band gap, and therefore can dramatically influence the performance of devices operating under irradiation conditions. They play an important role not only in the context of processes involving proton implants but also in all forms of radiation damage if, as is usually the case, hydrogen in introduced into the material in any subsequent processing step [1]. The origin of their activity is associated with Si dangling bonds within the vacancy and their partial passivation by hydrogen. The reaction between these radicals and H is strongly exothermic with energy gains of about 2–3 eV per Si–H bond. Such reaction might, if the concentration of H suffices, lead to the elimination of all such bonds, but in the usual case the concentration of hydrogen appears to be insufficient and the vacancy–hydrogen centres possess residual electrical activity.

The single vacancy in silicon is not stable at room temperature. It becomes mobile at ∼70 K (n-type silicon) or at ∼150 K (p-type silicon) and readily complexes both with other vacancies creating multi-vacancy centres, as well as with many impurities [2]. The divacancy (V_2) in silicon [3] is stable up to ∼220 °C when it becomes mobile. Despite efforts

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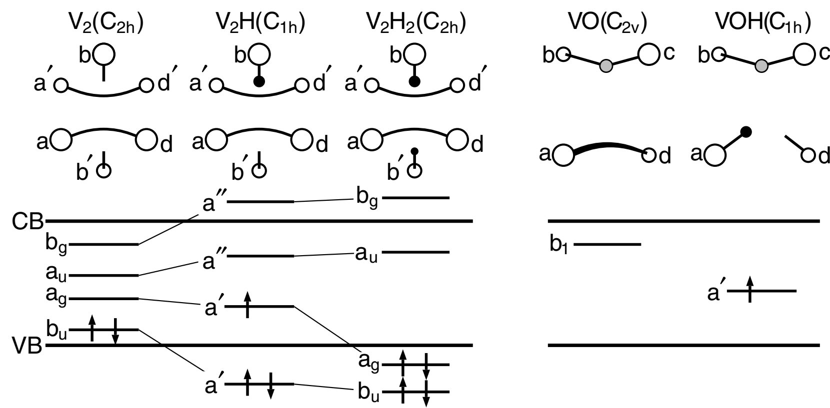

Figure 1. A schematic picture of the structures and one electron gap levels due to neutral V_2 (as proposed in [3]), V_2H and V_2H_2 complexes in Si (viewed along ⟨111⟩) and VO and VOH defects (viewed along ⟨100⟩). Levels are labelled according to the respective point group representations. Spin up/down occupancies are represented by upward/downward pointing arrows, respectively. Some complexes possess elongated but reconstructed Si_a–Si_d and $Si_{a'}$–$Si_{d'}$ bonds. Si, H and O atoms are shown as white, black and grey circles, respectively.

to theoretically describe this defect [4–6] several unanswered questions, such as those of its electrical properties and its annealing mechanism, remain. V_2 has single and double acceptor levels at 0.42 and 0.23 eV below the conduction band bottom (E_c), respectively, and a donor level at $E_v + 0.20$ eV [7, 8]. A curiosity is that in ion implanted Si, but not *e*-irradiated material, the amplitude of the 0.42 eV peak is greater than that of the 0.23 eV peak [7]. This suggests that there are additional defects with levels falling close to 0.42 eV.

In its ideal D_{3d} configuration, the neutral divacancy possesses six equivalent dangling bonds giving a half-filled e_u and an empty e_g levels in the gap. These are expected to provoke a Jahn–Teller distortion which drives two pairs of dangling bonds to reconstruct with elongated bonds, resulting in the C_{2h} structure shown on the left-hand side of figure 1. The Watkins and Corbett [3] interpretation of G6 and G7 electron paramagnetic resonance (EPR) signals (corresponding to V_2^+ and V_2^- respectively) was that the rebonding led to a splitting of the e states into a and b states as shown in the same figure. The electronic configurations for the positive and negative charge states are then $b_u^{\uparrow}$ and $b_u^{\uparrow\downarrow}a_g^{\uparrow}$ respectively. These configurations explain the large in-plane spin densities derived from the strong hyperfine splittings of the G6 and G7 EPR spectra [3]. Previous cluster calculations [5, 6] give support for this model but recent supercell calculations have been unable to predict these distortions probably because of the interaction between divacancies in different cells [4].

Of interest here are V_2H_n defects. EPR experiments on proton implanted floating-zone silicon (FZ-Si) samples revealed two monoclinic-I (C_{1h}) symmetric signals, labelled $S1_a$ and $S1_b$ and assigned to V_2H and V_3H complexes, respectively [9]. These signals could be observed at temperatures up to 230 °C, when they started to decay. Although their annealing mechanism is still unclear, we can compare their thermal stability with that of VH (180 °C [9]) or vacancy–oxygen–hydrogen (VOH) (260 °C [10, 11]) complexes. S1 spectra possess a rich set of ^{29}Si hyperfine satellites, and $S1_a$ showed a unique tiny proton hyperfine splitting. Similarities between the $S1_a$ signal—in particular its ^{29}Si hyperfine shoulders—and those arising from VH^0 [12] were explored; they suggested that the paramagnetic states are in many ways *similar* in the two defects [9].

A fingerprint of the V_2H complex has also been reported by using electrical techniques. High resolution Laplace deep level transient spectroscopy (LDLTS) measurements on H-diffused Si [11] and conventional DLTS experiments on proton implanted material [13] reported an electron trap at $E_c - 0.42$ eV (just over the $(-/0)$ levels of V_2 and VP complexes), which anneals at ∼200 °C. A good correlation between the annealing behaviour of the $E_c - 0.42$ eV trap and the $S1_a$ EPR signal has been shown in both works. Additionally, a deeper acceptor state at $E_c - 0.45$ eV (annealing out at ∼180) was linked to the VH defect [11, 13]. It should be noted that the $E_c - 0.45$ eV electron trap was previously assigned to a complex involving V_2 and hydrogen [14] and this is still a matter of dispute.

There is much less information from p-type material. It is however interesting to note that a decrease of the V_2 (0/+) peak is commonly observed in H-doped crystals (see for example [15, 16]). Although there is no evidence for a V_2H_n related hole trap, we cannot exclude the possibility of a scenario where its peak could be hidden by the signal from other defects, such as VOH or even V_2.

In this paper we will study the interaction between H and the divacancy in Si, concentrating on the electronic structure of V_2H and V_2H_2. A comparison of levels arising from V_2H_n complexes is made with those of other defects of interest such as VP, VO and VOH. Before reporting these results, we give a short description of our calculational procedures.

2. Method

We use a density-functional supercell code with localized s-, p- and d-like Cartesian–Gaussian basis functions on each atom [17] together with the Perdew–Wang exchange–correlation parametrization [18] and Bachelet–Hamann–Schlüter pseudopotentials [19]. 216 atom cells were employed and the Brillouin zone (BZ) sampled at the MP-2^3 special $\boldsymbol{k}$-point grid [20]. Further details are reported elsewhere [21].

Electrical levels were calculated according to the *marker method* [22]. Here the ionization energies and electron affinities of V_2H_n defects are compared with those of a defect (marker) with well established level locations. The method is most effective when the donor (or acceptor) state of the marker resembles that of the defect under investigation. Here we chose the VOH with donor and acceptor levels at $E(0/+) = E_v + 0.28$ and $E(-/0) = E_c - 0.32$ eV [11, 16, 23], and the vacancy–oxygen (VO) defect with an acceptor state 0.17 eV below E_c [24].

Details of VO and VOH complexes were previously reported in [25]. Their atomic and electronic structures are shown in figure 1. In this work we use a larger supercell though. These defects possess gap levels with distinct character. Inspection of the band structure from our supercell calculations reveals that while VOH produces a semi-occupied a' dangling bond state on a Si radical and oriented along a $\langle 111 \rangle$ direction, the VO complex induces an empty b_1 anti-bonding state edging the conduction band bottom and localized on its 3.093 Å length Si–Si elongated bond. The character of these states can be seen in figure 2.

As will become clear, we use the $(-/0)$ levels of VOH and VO as markers for acceptor levels of V_2H and V_2H_2 defects, respectively, while the donor level of VOH serves as a reference for investigating the donor activity of both complexes.

3. Results

There are two different ways of attaching H to a Si dangling bond in V_2. H binds either to one of the two Si atoms in the mirror plane or to one of the four equivalent Si atoms out of the mirror plane. The former defect with C_{1h} symmetry, shown in figure 1, turned out to

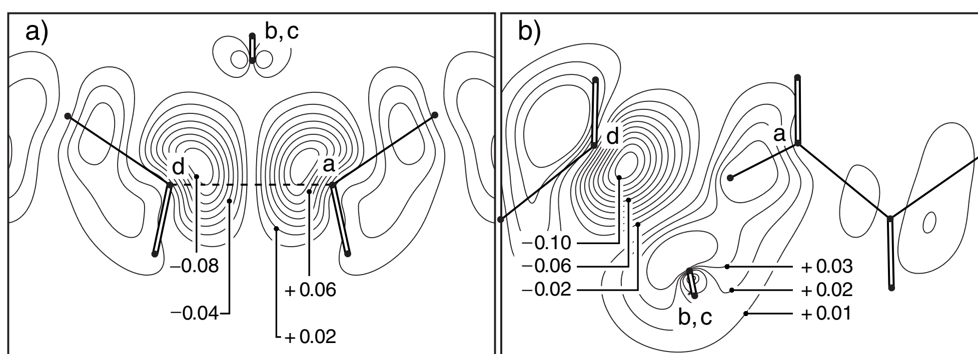

Figure 2. A contour plot of the Kohn–Sham orbital at Γ corresponding to the acceptor of VO (a) and donor/acceptor states of VOH defects (b), respectively. Both contour plots lie in the (110) plane. The atom labelling is according to figure 1.

possess the lower energy. The latter defect is not stable and recovered the C_{1h} symmetry upon relaxation. The neutral defect possesses a Si_b–H bond of length 1.509 Å, a $Si_{b'}$ radical in the mirror plane and two second neighbour Si_a–Si_d and $Si_{a'}$–$Si_{d'}$ reconstructed pairs with 2.761 and 2.824 Å bond lengths, respectively.

The reaction with a second proton at Si_d, $Si_{d'}$ or $Si_{b'}$ can form V_2H_2 complexes with C_{1h}, C_2 or C_{2h} symmetry, respectively. Our results indicate that two competitive structures exist: the C_{2h} form shown in figure 1 and the C_2 form which is metastable by 0.1 eV. Both defects possess two Si–Si second neighbouring reconstructions and the fact that all Si radicals are healed stabilizes the structures. The Si–H bond and Si–Si reconstruction lengths are 1.508 and 2.815 Å for the C_{2h} form and 1.506 and 2.953 Å for the C_2 form.

Now we analyse the electronic structure of these complexes. A schematic view of the one electron Γ states of V_2H and V_2H_2 is shown in figure 1 and compared with V_2. When H passivates Si_b in V_2, the b_u level is pushed below the valence band top, resulting in neutral V_2H possessing a singly occupied a' level localized at $Si_{b'}$. This state is *similar* (regarding its nature and wavefunction extent), to one produced by the VP or the VOH complex. Anti-bonding states (a_u and b_g) are only perturbed by the presence of H, but their symmetry changes to a$''$ with a nodal wavefunction in the mirror plane. The character of these states is *similar* to that of the gap state produced by the VO defect and their wavefunctions are localized on both Si_a–Si_d and $Si_{a'}$–$Si_{d'}$ reconstructed bonds, respectively. The latter is lower in energy and this ordering is due to the longer $Si_{a'}$–$Si_{d'}$ length.

In figure 3 we show a plot of the wavefunctions of the gap a' and a'' levels of V_2H. These can be readily compared with the marker levels shown in figure 2. The a' state (figure 3(a)) possesses a well localized dangling bond centred on the $Si_{b'}$ radical, whereas a'' (figures 3(b) and (c)) is an anti-bonding state between Si_a–Si_d and $Si_{a'}$–$Si_{d'}$. The Mulliken bond population analysis of the paramagnetic state of V_2H^0 (a') indicates an s-like spin localization of 5.3% on the $Si_{b'}$ radical and a total of 1.7% on Si_a and Si_d. Stallinga *et al* [9] reported several ^{29}Si hyperfine tensors from the $S1_a$ signal, among which two prominent shells with one and two equivalent Si atoms correspond to isotropic hyperfine components of −318.7 and −11.3 MHz, respectively. Comparing these with the 4594 MHz splitting from the Si 3s orbital we arrive to 6.9 and 0.2% of s-like localization on these shells, respectively. The agreement strongly suggests that the $S1_a$ signal arises from the neutral V_2H complex. Figure 1 also suggests the existence of a gap state produced by V_2H_2. Its character resembles that depicted in figures 3(b) and (c), but now it has recovered the higher a_u symmetry.

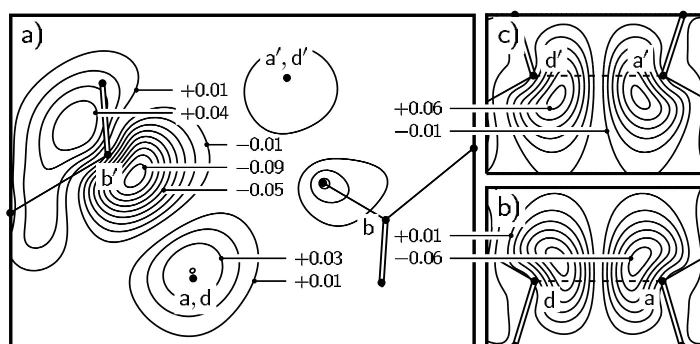

Figure 3. A contour plot of the Kohn–Sham orbital at Γ corresponding to the highest occupied level (a) and lowest unoccupied level (b), (c) of the neutral VH_2 defect in Si. Plot (a) lies in the (110) symmetry plane, whereas plots (b) and (c) lie on the $(1\bar{1}0)$ plane. The atom labelling is according to figure 1.

As mentioned in the previous section, electrical levels were calculated by comparing the ionization energy and electron affinity of V_2H and V_2H_2 with those of VOH and VO defects. Accordingly, we estimate that the (−/0) level of V_2H occurs about 0.1 eV deeper ($E(-/0) = E_c - 0.44$ eV) than that of VOH. Additionally, a (0/+) hole trap is estimated to be located 0.1 eV shallower than that of VOH, i.e., at $E_v + 0.18$ eV. The V_2H_2 complex was found to possess only an acceptor level lying at $E_c - 0.32$ eV. Unfortunately, due to the lack of accuracy of the calculation, we are not able to propose a definite assignment of V_2H to one of the two nearby electrical levels at $E_c - 42$ and $E_c - 45$ eV.

4. Conclusions

We find that H atoms can interact with the divacancy in Si, leading to the formation of V_2H and V_2H_2 complexes. Divacancies possessing more H atoms can exist but have not been considered here. There are significant differences between the energy levels of V_2H and V_2H_2 defects. Whereas V_2H possesses both a deep acceptor and deep donor activity, the V_2H_2 complex is only an acceptor. The levels of V_2H are located close to the (−/0) and (0/+) levels of the divacancy. Despite the lack of a DLTS peak in the lower half of the band gap, and suppression in hydrogenated material anti-correlated with the V_2 (0/+) level, we cannot rule out the possibility that a donor level of V_2H might be hidden by the peak of another defect level such as VOH or V_2. The character and extent of the neutral state of V_2H agree well with EPR experiments.

Finally we report an acceptor level at $E_c - 0.32$ eV arising from the V_2H_2 defect, with properties close to those of the acceptor state from the VO complex.

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