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Semiempirical electronic-structure calculations of hydrogen–phosphorus–vacancy complexes in crystalline silicon

Hongqi Xu

Department of Theoretical Physics, University of Lund, Sölvegatan 14A, S-22362 Lund, Sweden and Department of Solid State Physics and the Nanometer Consortium, University of Lund, Box 118, S-221 00 Lund, Sweden

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Abstract. We report on self-consistent calculations for the electronic structure of three hydrogen–phosphorus–vacancy complexes in crystalline silicon, based on a semiempirical tight-binding theory. These complexes, denoted by V-1H-3P, V-2H-2P, and V-3H-1P, consist of a vacancy and substitutional phosphorus impurities on the nearest-neighbour sites of the vacancy. The remaining silicon dangling bonds in the complexes are all saturated by hydrogen atoms. Each of the complexes is described by a large repeated supercell and we use the recursion method for computing local densities of states and orbital electron occupancies. We find that the three complexes do not introduce energy levels into the fundamental band gap, revealing that the electrical activity of the silicon dangling bonds can be well passivated by hydrogen atoms at bonding positions through strong orbital interactions and by phosphorus atoms at substitutional positions through Coulomb attractions. However, the complexes can have defect resonant states outside of the band gap. We show that these resonant states can be well described in terms of the symmetric combinations of the phosphorus orbitals and the symmetric combinations of the hydrogen and the hydrogen-saturated silicon orbitals.

1. Introduction

The topic of hydrogen in semiconductors has attracted a great deal of recent interest [1–3]. In silicon, the passivation of the group III acceptors, B, Al, and Ga, and of the group V donors, P and As, is well known and has been extensively studied [2, 3]. The microscopic structures of the hydrogen-shallow acceptor and hydrogen-shallow donor pairs, accounting for the mechanism of hydrogen passivation of shallow impurities, have been established, due to the strong interplay between theoretical calculations and experiments [2–12]. The hydrogen passivation of the deep-level defects in silicon has also been extensively studied experimentally [1, 3]. The theoretical calculations for the hydrogen-related complexes in these cases have, however, not been performed to the same extent as in the cases of the hydrogen-shallow impurity pairs. We report here the results of semiempirical electronic-structure calculations for the hydrogen–phosphorus–vacancy complexes in silicon.

In recent experimental study [13] by optical detection of magnetic resonance (ODMR), a di-hydrogen–vacancy (V-2H) complex in silicon was identified. In this treatment, a spin-triplet was observed. It was shown that the spin triplet is the

lowest electronic excited state of the V-2H defect in its neutral charge state, provided that the defect in the neutral charge state introduces two energy levels into the fundamental band gap and that the defect can have a negative charge state $(V-2H)^{1-}$ or a positive charge state $(V-2H)^{1+}$. Actually, the $(V-2H)^{1-}$ charge state has been observed in a study by deep-level transient spectroscopy (DLTS) and was labelled as the Z centre [14]. In a recent theoretical calculation [15], we showed that the V-2H defect does introduce two energy levels into the fundamental band gap and can indeed have $(V-2H)^{1-}$ and $(V-2H)^{1+}$ charge states. It was also shown, by both the ODMR experiment [13] and our theoretical calculations [15], that the two gap levels can be very well described by the silicon dangling bonds and that they have nearly zero contributions from the hydrogen and the hydrogen-saturated silicon orbitals. In addition, we have done calculations [15] for the other three hydrogen-vacancy complexes, namely mono-hydrogen-vacancy (V-1H), tri-hydrogen-vacancy (V-3H), and quadri-hydrogen-vacancy (V-4H) complexes in silicon. We have shown that the electrical activity remains also in the V-1H and V-3H defects and that the gap levels of these two defects also are basically silicon dangling-bond-like. For the V-4H defect, we have found, as was also demonstrated in a number of theoretical calculations [16–18], that the silicon-dangling-bond states of the isolated vacancy are well passivated by the four hydrogen atoms. In this paper, we will further show the ability of hydrogen to passivate the electrical activity of the phosphorus-vacancy complexes in silicon.

The interaction of atomic hydrogen with the silicon E centre was recently studied by infrared absorption [19]. It was shown that a number of complexes consisting of a silicon E centre and hydrogen atoms can be formed and the electrical activity of the silicon E centre can be partially or completely passivated by hydrogen atoms. So far, there is no experimental report on the complexes consisting of atomic hydrogen, a vacancy and more than one phosphorus atom. However, experimental evidence of complexes involving a vacancy and more than one phosphorus atom in heavily phosphorus-doped silicon has been previously reported [20]. Therefore, it is not entirely unexpected that the complexes consisting of atomic hydrogen, a vacancy and more than one phosphorus atom can be present in electron-irradiated hydrogenated, heavily phosphorus-doped crystalline silicon. We thus believe that the results of our electronic-structure calculations presented in this paper should be useful for further investigations of hydrogen-phosphorus-vacancy complexes in silicon.

The remainder of the paper is organized as follows: in section 2, we illustrate the atomic configurations of the hydrogen-phosphorus-vacancy complexes in silicon, studied in this paper. In section 3, an outline of the theoretical approach used in the calculations is presented. Section 4 contains the results of the calculations and a discussion in the light of our recent results of [15] for the V-4H complex and of [21] for the nearest-neighbouring substitutional quadri-phosphorus-vacancy (V-4P) complex in silicon. The paper is briefly summarized in section 5.

2. Configurations of hydrogen-phosphorus-vacancy complexes

In the present calculations, we examine the following three hydrogen-phosphorus-vacancy complexes: the mono-hydrogen-tri-phosphorus-vacancy, di-hydrogen-di-phosphorus-vacancy, and tri-hydrogen-mono-phosphorus-vacancy complexes in silicon. The three complexes are denoted by V-1H-3P, V-2H-2P, and V-3H-1P, respectively. The atomic configurations of these complexes are given in figure 1,

which shows the central cells of the defects, defined as a vacancy plus the hydrogen, phosphorus and hydrogen-saturated silicon atoms. In the present calculations, the hydrogen atoms are placed at a distance of 0.90 Å from the vacancy centre, while the phosphorus atoms and the hydrogen-saturated silicon atoms are placed at the non-distorted nearest-neighbour sites of the vacancy. These configurations give a silicon-hydrogen distance of 1.45 Å and hydrogen-hydrogen distance of 1.47 Å, presenting a reasonable value of the silicon-hydrogen bond length since this bond length in SiH₄ is 1.48 Å. In addition, it has been shown in [14] that with a theoretical approach similar to the present one this value (0.90 Å) of the distance between the hydrogen site and the vacancy centre causes the V-4H complex to restore well the electronic structure of the crystalline silicon [15]. The common feature of the three complexes is that the four silicon atoms around the vacancy either have an attached hydrogen atom or are replaced by a phosphorus atom.

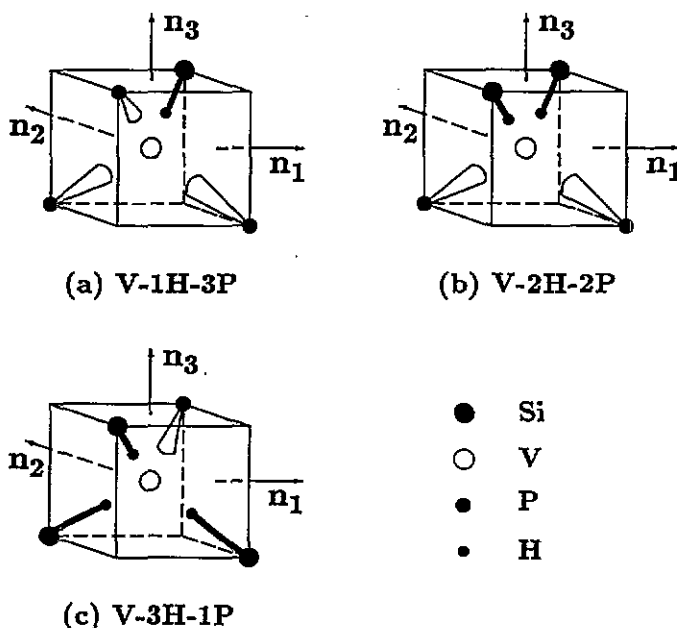


Figure 1. Schematic illustration of the proposed atomic configuration for (a) the mono-hydrogen-tri-phosphorus-vacancy (V-1H-3P) complex in C_{3v} symmetry, (b) the di-hydrogen-di-phosphorus-vacancy (V-2H-2P) complex in C_{2v} symmetry, (c) the tri-hydrogen-mono-phosphorus-vacancy (V-3H-1P) complex in C_{3v} symmetry in crystalline silicon. Only the central cells of the three complexes are shown in this figure.

3. Theoretical method

Our calculations are based on a self-consistent semiempirical tight-binding theory with the aid of the Wolfsberg-Helmholz formula for the orbital interactions [22] and the Sankey-Dow model of Coulomb effect for the electron-electron interactions [23]. The electronic structure of the perfect silicon crystal is described by an

sp^3 first- and second-nearest-neighbour tight-binding Hamiltonian [24]. In order to extract information about the electronic structure of the hydrogen–phosphorus–vacancy defects in the silicon crystalline environment, we use the repeated supercell approach [25] (2658 silicon atoms plus the atoms in the central cell of the defect in each supercell). The electron occupations of orbitals and the changes in the local densities of states induced by the defects are calculated using the quadrature approach of Nex [26] and the continued-fraction approach of Haydock *et al* [27], respectively, within the recursion method (a real-space Green's function method) [28].

For a defect system, the Hamiltonian can be formally expressed as $H = H_0 + U$, where H_0 is the Hamiltonian of the perfect system and U stands for the defect potential. In the present calculations, we assume that the defect potential U has non-zero matrix elements only for the vacancy and the atoms in the central cell of the defect plus the second-nearest-neighbour sites of the vacancy. For the vacancy site, the matrix elements of U are treated with a standard procedure equivalent to decoupling the atomic orbitals on the vacancy site from the solid. For the atoms in the central cell of the defect and at the second-nearest-neighbouring sites of the vacancy, the off-diagonal matrix elements of the Hamiltonian H are expressed in terms of orbital interactions with the Wolfsberg–Helmholz formula [22] and are deduced from the off-diagonal matrix elements of the perfect-crystal Hamiltonian H_0 , while the diagonal matrix elements of H are assumed to be dependent on the electron occupations of orbitals and are, therefore, calculated self-consistently with the Sankey–Dow model [23]. We note here that for the hydrogen atoms, only the s orbitals are important and are included in our sp^3 basis, because the energy of the p orbitals is much higher than that of the s orbitals. We note also that for the silicon atoms which are the first nearest neighbours of the phosphorus atoms, the diagonal matrix elements are simply approximated by the values self-consistently determined for the V-4P complex in silicon [21], while for the silicon atoms which are the first nearest neighbours of the hydrogen-saturated silicon atoms, the diagonal matrix elements are simply approximated by the values self-consistently determined for the V-4H complex in silicon [15]. Further details of the theoretical approach can be found in [15, 29].

4. Computational results

We shown in figure 2 the calculated changes in the local densities of states (LDOS) induced by the three hydrogen–phosphorus–vacancy complexes, V-1H-3P, V-2H-2P, and V-3H-1P, in silicon corresponding to the symmetric combinations of the atomic orbitals centred on the atomic sites in the central cell of the defect. In order to have a better understanding of the calculated electronic structure of the three defects, we also show in this figure the calculated changes in the LDOS for the V-4P and V-4H complexes in silicon. The details of the computational results for these two defects (V-4P and V-4H) can be found elsewhere [15, 21]. In this figure we have not, however, shown the calculated results of a_2 symmetry (in C_{3v}) for V-1H-3P and V-3H-1P and of a_2 symmetry (in C_{2v}) for V-2H-2P, since no significant changes in the LDOS occur in these cases.

Figure 2 shows clearly that the three hydrogen–phosphorus–vacancy complexes do not introduce any energy levels into the fundamental band gap in silicon. We predict that for the three defects in the neutral charge states, the valence band is

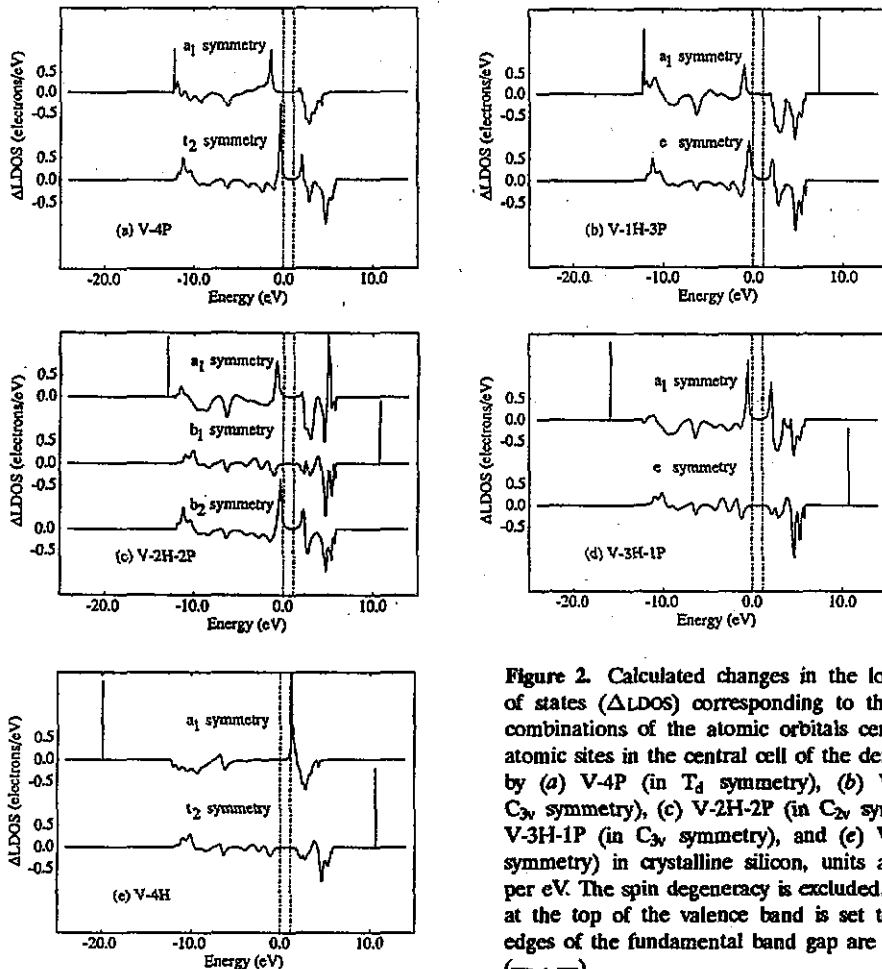


Figure 2. Calculated changes in the local densities of states (Δ LDOS) corresponding to the symmetric combinations of the atomic orbitals centred on the atomic sites in the central cell of the defect, induced by (a) V-4P (in T_d symmetry), (b) V-1H-3P (in C_{3v} symmetry), (c) V-2H-2P (in C_{2v} symmetry), (d) V-3H-1P (in C_{3v} symmetry), and (e) V-4H (in T_d symmetry) in crystalline silicon, units are electrons per eV. The spin degeneracy is excluded. The energy at the top of the valence band is set to zero. The edges of the fundamental band gap are identified by (— · —).

fully occupied with electrons and the conduction band is empty, showing that the three defects are electrically inactive centres.

Some similar features can be seen in the calculated electronic structures of the defects. The changes in the LDOS of e symmetry (in C_{3v}) of V-1H-3P and of b_2 symmetry (in C_{2v}) of V-2H-2P resemble closely the change in the LDOS of t_2 symmetry (in T_d) of V-4P, and are characterized by the three peaks, two at the edges of the valence band and one at the bottom of the conduction band, corresponding to the three resonance states. The localizations of the three resonance states have been estimated using the recursion method within the square-root termination approach [27, 28]. It has been found that the resonance state at the bottom of the valence band has largely phosphorus s character, while the resonance state at the top of the valence band is largely built from the phosphorus p orbitals. Both of the two states are rather localized. However, the resonance state at the bottom of the conduction band is somewhat delocalized. For example, for the V-4P complex only $\sim 7\%$ ($\sim 16\%$) of the wavefunction of this resonance state is found to be localized on the phosphorus s (p) orbitals. The three resonance states have nearly zero contributions from the

hydrogen and hydrogen-saturated silicon atomic orbitals. Compared to the calculated changes in the LDOS of t_2 symmetry (in T_d) of the isolated ideal vacancy in silicon (see figure 3(f) in [15]), the spectra of e symmetry of V-1H-3P, b_2 symmetry of V-2H-2P, and t_2 symmetry of V-4P reflect a shift of energy levels towards lower energies caused by replacing the neighbouring silicon atoms of the vacancy by the phosphorus atoms. Therefore, the resonance state at the top of the valence band can be considered as derived from the t_2 gap state of the isolated vacancy.

The changes in the LDOS of b_1 symmetry (in C_{2v}) of V-2H-2P and of e symmetry (in C_{3v}) of V-3H-1P, on the other hand, appear to resemble well the changes in the LDOS of t_2 symmetry (in T_d) of V-4H. We have found that for the symmetries considered here, the V-2H-2P and V-3H-1P complexes have a defect state at an energy well above the (lowest) conduction band. This state can be considered as an antibonding state built purely from the hydrogen s orbitals and the hydrogen-saturated silicon hybrids, since over 90% of its wavefunction is found to be accounted for by these orbitals. Our calculations predict that the two hydrogen atoms in V-2H-2P restore well the silicon crystalline valence states of b_1 symmetry in C_{2v} and the three hydrogen atoms in V-3H-1P restore well the crystalline valence states of e symmetry in C_{3v} , although for each of the two complexes a very weak resonance state (b_1 symmetric for V-2H-2P or e symmetric for V-3H-1P) may still be seen at the bottom of the valence band. These results indicate that the silicon dangling-bond gap states have been pushed into the valence band due to the interactions with the hydrogen s orbitals, and the silicon-hydrogen bonding states resulting from the interaction recover well the corresponding silicon-silicon bonding states of the silicon crystal.

The changes in the LDOS of a_1 symmetry (in C_{3v}) induced by V-1H-3P and V-3H-1P and of a_1 symmetry (in C_{2v}) induced by V-2H-2P may look more complicated than the cases we discussed above. It has been found that these changes in the LDOS have large contributions from the a_1 symmetric (in C_{2v} or C_{3v}) combinations of both the phosphorus orbitals and the hydrogen-silicon bonding and antibonding states. Three localized a_1 states are introduced by each of the three hydrogen-phosphorus-vacancy complexes. The a_1 resonance state at the top of the valence band is mainly built from the phosphorus atomic p orbitals and has hardly any of the orbital character of the hydrogen atoms and the hydrogen-saturated silicon atoms. This state, therefore, corresponds to the a_1 (in T_d) resonance state of V-4P at the top of the valence band. It can be seen, in the energy spectra of the three hydrogen-phosphorus-vacancy complexes and the V-4H complex, that the energy of the a_1 state is slightly increased as the number of phosphorus atoms in the complexes is decreased. This is just what one would expect, because the a_1 state induced by V-2H-2P, V-1H-3P or V-4P can simply be viewed as a state formed by adding together the phosphorus p orbitals pointing towards the vacancy centre in the defect and the energy of the state is, therefore, lowered approximately from the energy of the single phosphorus p orbital pointing towards the vacancy centre (i.e., the energy of the a_1 resonance state at the top of the valence band induced by V-3H-1P) by $|E_{pp}|$, $2|E_{pp}|$ and $3|E_{pp}|$ for V-2H-2P, V-1H-3P, and V-4P, respectively where E_{pp} denotes the interaction energy between the two phosphorus p orbitals pointing towards the vacancy centre and is negative.

The lowest and highest a_1 defect states induced by each of the three hydrogen-phosphorus-vacancy complexes are, however, mainly built from the hydrogen s orbitals and the hydrogen-saturated silicon orbitals and, therefore, correspond to

the two a_1 states (in T_d) of V-4H. These two a_1 states shift towards lower energies as the number of hydrogen-silicon atomic pairs in the defect is increased. This can be understood in the same way as for the a_1 resonance state at the top of the valence band of the three complexes. We note here that the a_1 defect state of V-3H-1P in the conduction band are found to have very similar orbital character of the phosphorus atoms. This is due to the facts that the a_1 symmetric combinations of the phosphorus orbitals in the V-1H-3P complex become more similar to the corresponding a_1 symmetric combinations of the phosphorus orbitals in V-4P than those in V-2H-2P and V-3H-1P, and that the single phosphorus p orbital pointing towards the vacancy centre in the V-3H-1P complex contains the defect character of both a_1 and t_2 symmetries of the V-4P complex. We remind the reader that the V-4P complex has a very localized a_1 defect state at the bottom of the valence band and a t_2 resonance state in the conduction band, in addition to the a_1 and t_2 defect states at the top of the valence band.

The results of our calculations for the three hydrogen-phosphorus-vacancy complexes in silicon indicate that the interactions between the phosphorus atomic orbitals and the hydrogen-silicon bonding and antibonding states have minor effects on the electronic structure of the complexes. The essence of the hydrogen atoms in the complexes is to decouple the interactions of the silicon dangling bonds with other orbitals and to remove the corresponding silicon dangling-bond states from the fundamental band gap, suggesting that the ability of hydrogen to passivate the electrical activity of silicon dangling bonds does not depend on the lattice environment. The role of the phosphorus atoms in the complexes is simply to lower the energies of the dangling bonds of the vacancy and thus the energies of the corresponding defect states.

5. Summary

In this paper, we have predicted that the V-1H-3P, V-2H-2P, and V-3H-1P complexes in silicon do not introduce any energy levels into the fundamental band gap and are all electrically inactive. We have found that the electronic structures of e symmetry of V-1H-3P and of b_2 symmetry of V-2H-2P closely resemble the electronic structure of t_2 symmetry of V-4P, while the electronic structures of b_1 symmetry of V-2H-2P and of e symmetry of V-3H-1P closely resemble the electronic structure of t_2 symmetry of V-4H. The electronic structures of the a_1 symmetries of the three hydrogen-phosphorus-vacancy complexes are found, however, to have the defect characters of both V-4P and V-4H. We have shown that the localised defect states of the three complexes are all accounted for in terms of symmetric combinations of the phosphorus atomic orbitals and the symmetric combinations of the hydrogen s orbitals and the hydrogen-saturated silicon atomic orbitals. The interactions of the phosphorus orbitals with the hydrogen and hydrogen-saturated silicon orbitals have minor effects on the electronic structure of the three complexes. Our calculations demonstrate clearly that the electrical activity of the silicon dangling bonds can be well passivated by hydrogen atoms at bonding positions through strong orbital interactions and by phosphorus atoms at substitutional positions through Coulomb attractions. We believe that the results of the present calculations are very typical for the electronic structure of the hydrogen-group V impurity-vacancy complexes in silicon. We, therefore, suspect rather similar results for hydrogen-arsenic-vacancy and hydrogen-antimony-vacancy complexes in silicon.

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