

Si-P-H complexes in crystal silicon: A theoretical study

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Complexes formed by silicon, hydrogen, and phosphorus atoms in crystalline silicon have been studied by an *ab initio* Hartree-Fock method in a cluster approach. Three hydrogen equilibrium sites have been obtained, with quite different passivation efficiencies. An estimate of the bending- and stretching-mode energies of the hydrogen atom is obtained by an analysis of the cluster normal modes. Finally, an additional local minimum in boron-doped silicon is reported.

Hydrogen passivation of donors in crystalline silicon, previously observed by Johnson *et al.*,¹ has been recently shown² to be as strong as the most widely known acceptor passivation.^{3,4} Far-infrared vibrational spectra in hydrogenated P-, As-, and Sb-doped silicon show that the electrical neutralization of these impurities takes place through hydrogen-donor-complex formation.² The lack of dependence on donor species of the energy of two hydrogen-induced absorption lines² and the trigonal symmetry shown by the splitting under uniaxial stress of these lines⁵ suggest a stable equilibrium position for H at the antibonding site of a silicon-atom nearest neighbor of the donor atom (ab-Si, see Fig. 1).

This experimental evidence agrees with the results of an earlier semiempirical tight-binding study in P-doped silicon,¹ confirmed by a more sophisticated first-principles supercell approach.⁶ The latter finds two additional local minima, at the impurity-antibonding *ab-i* site and at the bond-centered *bc* site, see Fig. 1. The energy values corresponding to these two minima are 0.57 and 1.13 eV higher than that of the absolute minimum, respectively. In this supercell approach, the *ab-Si* site is located as much as 2.33 Å from the nearest Si—i.e., 0.02 Å from the tetrahedral site *T*—and is characterized by a weak Si—H bond. The estimated energy for the H stretching mode is therefore much lower (400 cm⁻¹) than the measured experimental values (1555 and 809 cm⁻¹ for the stretching and the bending mode, respectively, see Ref. 2).

An alternative approach can be tried in the framework of an *ab initio* Hartree-Fock method by reproducing the local environment around the hydrogen and the impurity atoms in a suitable molecular cluster extracted from the silicon matrix. Close values are indeed measured for the Si—Si bond length in disilane (2.33 Å) (Ref. 7) and in *c*-Si (2.35 Å),⁸ and for the Si—H stretch vibrational energy in silane (2189 cm⁻¹) (Ref. 9) and in annealed hydrogenated silicon (2060 cm⁻¹).¹⁰ These chemical bonds can therefore be adequately described in *c*-Si in terms of a local environment picture. Moreover, the Hartree-Fock method accurately reproduces the structure of molecules, as will

be shown in the following for the disilane, silane, and phosphine cases. Similar arguments have justified, in the past, the use of the Hartree-Fock method and a cluster approach in the investigation of structural properties of covalent semiconductors. In the present context this method may therefore provide a sound support to the understanding of the experimental findings, while complementing the supercell method. The cluster approach actually underestimates solid-state effects, whereas the supercell method cannot avoid impurity interaction effects, unless exceedingly large cells are used. Preliminary results¹¹ obtained by Hartree-Fock total-energy calculations in a Si₁₀PH₂₆ cluster (Si and P atoms 1–11 in Fig. 1) only in part agree with those reported in Ref. 6. In particular, a much shorter Si—H distance (1.41 Å) for the *ab-*

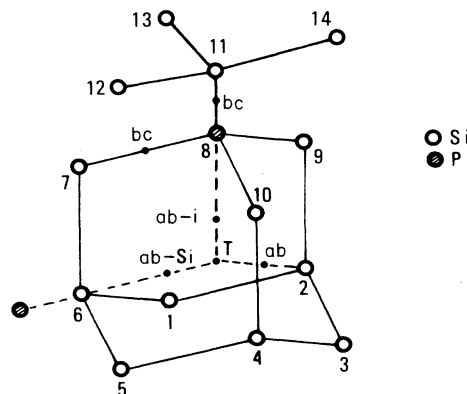


FIG. 1. Schematic view of the cluster and the sites studied in this work. Si atoms are numbered 1–7 and 9–14; the P atom is number 8. An additional P atom, not part of the investigated cluster, has been added for the sake of clarity. The hydrogen sites shown in this figure are the bond-centered site *bc*, the tetrahedral site *T*, the antibonding site *ab*, the antibonding site on the impurity side *ab-i*, and the antibonding site of a silicon-atom nearest neighbor of the donor atom (*ab-Si*).

Si configuration, and a reversed energy ordering for the *ab-i* and *bc* configuration, is obtained.¹¹ A more detailed investigation of the H-P complex, thus, has been performed in order to check these preliminary results, to obtain an estimate of the far-infrared vibration modes and to get a qualitative understanding of the donor passivation mechanism.

In the present work the equilibrium configurations of different thoroughly relaxed Si-H-P complexes have been investigated in a $\text{Si}_{13}\text{PH}_{32}$ cluster (Si and P atoms 1–14 in Fig. 1) whose surface has been saturated by H atoms placed at 1.49 Å from the outer silicon atoms.¹² This larger cluster allows a better description of the impurity environment than that obtained in the 10-silicon-atom cluster previously investigated. All calculations have been carried out on the Cray Research, Inc. X-MP/48 supercomputer at Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale by means of the GAUSSIAN-86 program¹³ and by the Fletcher-Powell energy-minimization procedure.¹⁴ The STO-3G (STO denotes Slater-type orbital; G stands for Gaussian) basis set¹⁵ has been extensively used, while the larger 6-31G basis set¹⁶ has been utilized to get an estimate of the H vibration modes.

The absolute energy minimum is found for hydrogen at an *ab-Si* site located 1.41 Å away from the Si atom. The Si and P atoms nearest neighbors of the H atom move by 0.63 and 0.09 Å from their unrelaxed positions, which results in a Si-P distance equal to 3.07 Å and in a quasiplanar configuration for the Si tetrahedral umbrella. A local minimum—0.19 eV higher in energy—is attained for hydrogen at a *bc* site placed at 1.39 and 2.04 Å from the nearest Si and P atoms, respectively. Finally, a local minimum—2.37 eV higher in energy—is found for hydrogen at an *ab-i* site, 1.43 Å away from the P atom. These results closely match those obtained for the *bc* configuration in a $\text{Si}_7\text{PH}_{19}$ cluster (Si and P atoms 7–14 in Fig. 1) and those already achieved in the $\text{Si}_{10}\text{PH}_{26}$ cluster,¹¹ thus pointing to negligible cluster size effects.

The estimate of the far-infrared—mode energies strongly depends on the choice of the basis set, as will be shown in the following. Several basis sets¹⁷ have been tested by comparing the computed and experimentally observed equilibrium geometries and vibrational mode energies of a few simple molecules. In particular, silane, disilane, and phosphine molecules—the simplest prototypes of hydrogenated Si:P—have been investigated. The values for the equilibrium bond lengths and angles of these three molecules are described within a few percent by all the tested basis sets. The vibrational mode energies have been evaluated only for the STO-3G and 6-31G basis sets, which give slightly better equilibrium geometries: in particular, the Si—Si and the Si—H bond lengths in disilane are equal to 2.38 and 1.49 Å, respectively, as evaluated with the 6-31G basis set, to be compared with the corresponding experimental values of 2.33 Å (Ref. 7) and 1.48 Å.¹⁸ The estimated mode energies, however, strikingly differ for these two basis sets: as an example, in the silane molecule the STO-3G, 6-31G, and experimental values¹⁹ are, respectively, 2929, 2277, and 2273 cm^{-1} for the stretching mode and 1170, 960, and 929 cm^{-1} for the

bending mode.

In P-doped silicon the more reliable 6-31G basis set has given an energy of 2149 cm^{-1} for a stretching mode of A_1 symmetry and of 908 cm^{-1} for a doubly degenerate bending mode of E symmetry, respectively, when the hydrogen atom sits at the *ab-Si* site. These results have to be compared with the infrared lines observed at 1555 and 809 cm^{-1} and attributed to the vibrational modes of a hydrogen atom at the same site. A satisfactory agreement is obtained for the bending-mode energy. The lack of an agreement for the stretching-mode energy points instead to a Si-H interaction weaker than that suggested by the present results. An analysis of the electronic charge distribution performed using Mulliken population analysis²⁰ shows a strong Si-H interaction slightly perturbed by a weak Si-P interaction, which is responsible for the small decrease of the Si—H stretching energy with respect to the silane case. A better description of the H-Si-P complex could be obtained by using a richer basis set which includes d valence atomic orbitals for the Si and P atoms.²¹ This would strengthen a three-center interaction, resulting in a less uneven interaction of the Si atom with its H and P partners, in agreement with the experimental results. Somewhat opposite conclusions have been obtained in the supercell approach, resulting in a stretching-mode energy much lower (400 cm^{-1}) than the experimental value.^{6–22}

Further understanding of the hydrogen equilibrium geometries can be achieved by comparing the present results with those already obtained by the same theoretical approach in pure and boron-doped silicon. In pure silicon the absolute energy minimum is found for H at the *bc* site, while a local minimum is obtained at the T site.²³ The introduction of a substitutional impurity perturbs in a different way the total-energy topography around these two sites. The *bc* site, as to equilibrium conditions, is an absolute minimum in boron-doped silicon^{6,24–26} and transforms into a local one in phosphorus-doped silicon. The T region is more drastically perturbed by the presence of the impurity. In Si:P the local minimum at T evolves into two different *ab* sites—*ab-Si* and *ab-i*—the former now being the absolute minimum and the latter a local one, as discussed above. In Si:B the T region seems instead to be completely destabilized, at least for the high-symmetry sites investigated so far, the T and the *ab-i* ones.^{6,24–26} However, an investigation performed here on the *ab-Si* site leads to a local minimum at 1.40 Å from the silicon atom, 2.45 eV higher than the absolute minimum. This new theoretical result is in excellent agreement with a recent channeling experiment in Si:B, which locates 17% of the H atoms at an *ab-Si* site, 1.2–1.5 Å away from the Si atom.²⁷ All these features can be related to the different valence of donors and acceptors. The lower valence of B atoms with respect to Si atoms favors a three-center interaction at the *bc* site; the higher valence of P atoms instead promotes fivefold-coordinated configurations, as those obtained at the *ab-i* site and at the *ab-Si*.

For what concerns passivation effects, it should be mentioned that, due to the neglect of solid-state effects, the present approach does not allow an accurate descrip-

tion of the electronic properties of an impurity in the silicon matrix. Nevertheless, some suggestions on the passivation mechanisms come from the following simplified picture: the electronic donor level in the P-doped silicon band gap is attributed to an electron weakly bound to the donor, the passivation to a reinforcement of this electronic binding. The strength of this binding has been investigated for several Si-P complexes, with and without hydrogen, by an analysis of the electronic charge distribution performed by the Mulliken population analysis.²⁰ In absence of hydrogen, the resulting picture is well accounted for by the valence three of the phosphorus atom. Three of the five P valence electrons indeed form bonds with the nearest-neighbor silicon atoms, while a weak antibonding character is found for the bond with the fourth silicon atom. The last two P valence electrons are arranged in an atomiclike $3p$ lone pair. This lone pair is the most likely counterpart of the donor level. In presence of hydrogen, the atomic arrangements found for the Si-H-P complexes have different effects on the electronic binding. In the bc case the electronic charge distribution is virtu-

ally unaffected by the insertion of hydrogen, thus suggesting that passivation does not take place. In the ab-*i* geometry, the two lone-pair electrons form bonds with the H and the fourth Si atoms, according to the five valence electrons for the phosphorus atom. This strong binding of the lone-pair electrons corresponds to donor passivation. In the most stable ab-Si configuration a weak bond replaces the antibonding feature observed in absence of hydrogen. The two lone-pair electrons are only involved in part in the bond formation, possibly resulting in the donor passivation experimentally observed and already theoretically predicted.^{1,2,6}

Note added in proof. We have only now become aware that D. Tripathi *et al.* report [Phys. Rev. B (to be published)] on a Si-H mode energy in P-doped silicon whose experimental value is equal to about 2100 cm^{-1} , in very good agreement with our theoretical result.

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- ¹N. M. Johnson, C. Herring, and D. J. Chadi, Phys. Rev. Lett. **56**, 769 (1988).
- ²K. Bergman, M. Stavola, S. J. Pearton, and J. Lopata, Phys. Rev. **37**, 2770 (1988).
- ³J. I. Pankove, D. E. Carlson, J. E. Berkeyheiser, and R. O. Wance, Phys. Rev. Lett. **51**, 2224 (1983); J. I. Pankove, P. J. Zanzucchi, C. W. Magee, and G. Lucovsky, Appl. Phys. Lett. **46**, 421 (1985).
- ⁴C.-T. Sah, J. Y.-C. Sun, and J. J.-T. Tzou, Appl. Phys. Lett. **43**, 204 (1983).
- ⁵S. J. Pearton, M. Stavola, and J. W. Corbett, in Proceedings of the Fifteenth International Conference on Defects in Semiconductors, Budapest, 1988 [Mater. Sci. Forum (to be published)]; K. Bergman, M. Stavola, S. J. Pearton, and T. Hayes, Phys. Rev. B **38**, 9643 (1988).
- ⁶K. J. Chang and D. J. Chadi, Phys. Rev. Lett. **60**, 1422 (1988).
- ⁷B. Beagley, A. R. Conrad, J. M. Freeman, J. J. Monaghan, and B. G. Norton, J. Mol. Struct. **11**, 371 (1972).
- ⁸W. Parrish, Acta Crystallogr. **13**, 838 (1960).
- ⁹H. W. Kattenberg and A. Oskam, J. Mol. Spectrosc. **49**, 52 (1974).
- ¹⁰H. J. Stein, Phys. Rev. Lett. **43**, 1030 (1979).
- ¹¹A. Amore Bonapasta, A. Lapicciarella, N. Tomassini, and M. Capizzi, in Proceedings of the Fifteenth International Conference on Defects in Semiconductors, Budapest, 1988 [Mater. Sci. Forum (to be published)].
- ¹²A. Amore Bonapasta, C. Battistoni, A. Lapicciarella, N. Tomassini, S. L. Altmann, and K. W. Lodge, Phys. Rev. B **37**, 3058 (1988); S. Estreicher, A. K. Ray, J. L. Fry, and D. S. Marynick, Phys. Rev. Lett. **55**, 1976 (1985).
- ¹³GAUSSIAN-86, M. J. Frisch, J. S. Brinkley, H. B. Schlegel, K. Ragavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. Defrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder, and J. A. Pople, Carnegie Mellon Quantum Chemistry Publications Unit, Carnegie Mellon University, Pittsburgh, PA, 1984.
- ¹⁴M. Fletcher and M. J. D. Powell, Comput. J. **6**, 163 (1963).
- ¹⁵W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **52**, 2769 (1970).
- ¹⁶W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys. **56**, 2257 (1972); P. C. Hariharan and J. A. Pople, Theor. Chem. Acta **28**, 213 (1973).
- ¹⁷The following basis sets have been used: the STO-3G, the 6-31G, and the Huzinaga (4321/421) and (43111/4111) sets; see S. Huzinaga, in *Gaussian Basis Sets for Molecular Calculations* (Elsevier, Amsterdam, 1984).
- ¹⁸J. H. Callomon, E. Hirota, K. Kukitzu, D. J. Lafferty, E. G. Maki, and C. S. Pate, in *Structural Data on Free Polyatomic Molecules*, Landolt Börnstein New Series, edited by K. H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, 1976), Gp. II, Vol. 7.
- ¹⁹These values have been taken from W. D. Allen and H. F. Schaefer III, Chem. Phys. **108**, 243 (1986), where anharmonicity effects have been eliminated from the experimental values.
- ²⁰R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).
- ²¹The inclusion of the *d* valence atomic orbitals has to be performed together with a careful basis-set balance, comprehensive of the atoms on the cluster surface.
- ²²It may be worth noticing that the tight-binding method has found a Si—H bond-length value of 1.61 \AA and a vibrational-mode energy value of 2145 cm^{-1} for H at an ab-Si site (see Ref. 1).
- ²³A. Amore Bonapasta, A. Lapicciarella, N. Tomassini, and M. Capizzi, Europhys. Lett. **7**, 145 (1988).
- ²⁴G. G. DeLeo and W. B. Fowler, Phys. Rev. B **31**, 6861 (1985).
- ²⁵A. Amore Bonapasta, A. Lapicciarella, N. Tomassini, and M. Capizzi, Phys. Rev. B **36**, 6228 (1987).
- ²⁶P. J. H. Denteneer, C. G. Van de Walle, Y. Bar-Yam, and S. T. Pantelides, in Proceedings of the Fifteenth International Conference on Defects in Semiconductors, Budapest, 1988 [Mater. Sci. Forum (to be published)].
- ²⁷A. D. Marwick, G. S. Oehrlein, J. H. Barrett, and N. M. Johnson, MRS Symp. Proc. **104**, 259 (1988).