PHYSICAL REVIEW B VOLUME 42, NUMBER 5 15 AUGUST 1990-I

Vibrational frequencies of Si-P-H complexes in crystalline silicon: A theoretical study

A. Amore Bonapasta and P. Giannozzi
Institut Romand de Recherche Numérique en Physique de Matériaux (IRRMA), Ecole Polytechnique Fédérale de Lausanne, PHB-Ecublens, CH-1015 Lausanne, Switzerland

M. Capizzi
Dipartimento di Fisica, Università degli Studi di Roma "La Sapienza," piazzale Aldo Moro 2, I-00185 Roma, Italy

(Received 26 January 1990; revised manuscript received 29 March 1990)

Atomic complexes formed by silicon, hydrogen, and phosphorus in crystalline silicon have been studied by using the pseudopotential-density-functional method in a supercell approach. The bending and the stretching H mode energies have been estimated for the stable and the metastable sites of the H atom. Their values for the stable H site (i.e., the antibonding silicon one) are in very good agreement with those of two infrared-absorption lines.

The passivation of acceptors and donors observed in hydrogenated crystalline silicon has been the object of a great number of experimental and theoretical investigations.[1–15] Infrared- (ir-) vibrational spectra have shown that the electrical neutralization of shallow impurities takes place through the formation of silicon-hydrogen-impurity complexes;[1,2,6,7,9] the splitting under uniaxial stress of the ir-absorption lines has given evidence of a trigonal symmetry for the stable equilibrium position of the H atom.[4] Experimental values for the vibrational energies, reported by several authors, coincide for the acceptor-hydrogen-silicon complexes and strongly disagree for the donor ones.[6,7]

The H equilibrium positions and the vibrational frequencies for the corresponding complexes have been investigated by using somewhat alternative theoretical methods: the pseudopotential-density-functional[10,13] (PPDF) or an empirical tight-binding[9] (TB) method, in a supercell approach, and different approximation schemes[8,11,12,14,15] to the Hartree-Fock (HF) method, in a cluster approach. In the acceptor case (e.g., boron), the absolute energy minimum for H has been anyway found at the bond-center site (BC in Fig.1).[8] Excellent agreement has also been obtained between experimental and theoretical estimates of the Si-H-B vibrational frequencies.[8] In the donor case (e.g., phosphorus), the same theoretical methods have found the H stable equilibrium position at the antibonding silicon site (AB-Si in Fig. 1). This nicely agrees with the observation, in hydrogenated Si:P, of an independence of the energy of the absorption lines on the impurity species.[6] However, TB, HF, and PPDF computational frameworks[8,9,13,15] have resulted in different values for the H-Si-P vibrational energies, which are listed in Table I together with their experimental counterparts. This corresponds to a different Si-H interaction, also confirmed by the difference in the bond-length values (see Table I). Si—H bond lengths (vibrational frequencies) evaluated in the TB and HF methods are indeed shorter (higher) than those estimated in the PPDF one. Therefore, neither the theoretical nor the experimental findings have yet resulted in an unambiguous description of the H-Si-P complex structure, although some preliminary PPDF calculations[8] seem to converge toward the results reported in Ref. 6.

In the present work, the equilibrium configurations of Si-H-P complexes have been investigated in the Hohenberg-Kohn density-functional-theory framework[16] by using the Kohn-Sham local-density approximation[16,17] with the Ceperley-Alder exchange-correlation-data[18] and norm-conserving pseudopotentials[19] in a plane-wave basis set;[17] k-space integration has been performed with use of the special-points technique.[20] The pseudopotentials used for P and H have the same form as for Si,[21] with proper parameters.[22] These pseudopotentials have been tested by estimating the equilibrium

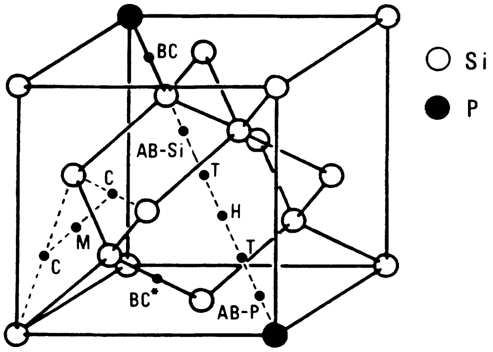

FIG. 1. Hydrogen sites studied in the present work: the antibonding site of a silicon-atom nearest neighbor of the donor atom, AB-Si; the antibonding site on the impurity side, AB-P; the bond-centered sites, BC and BC*; the tetrahedral site, T; the hexagonal site, H; the C site; and the M site.

TABLE I. Different theoretical estimates for the Si-P-H complex geometries and for the vibrational energy values of the H atom located at the AB-Si site. Atomic displacements from the unrelaxed positions are assumed to have a positive sign whenever the atom moves in the [111] direction from the P atom toward the Si one (see Fig. 1). Values of the ir-absorption lines observed in hydrogenated Si:P are also reported in the last two lines.

Methods	ΔP (Å)	ΔSi (Å)	H-Si (Å)	P-Si (Å)	$\tilde{\nu}_s$ (cm^{-1})	$\tilde{\nu}_b$ (cm^{-1})	Ref.
HF[a]	−0.54	0.67	1.44	3.56	2140	630	8
HF	−0.19	0.74	1.40	3.28			12
HF	−0.09	0.63	1.41	3.07	2149	908	15
TB[b]			1.61		2145		9
PPDF[c]	−0.05	0.09	2.33	2.49	400		13
Expt.					1555	809	6
Expt.					~2100		7

[a] HF: Hartree-Fock cluster approach.
[b] TB: tight-binding supercell approach.
[c] PPDF: pseudopotential-density-functional supercell approach.

geometries of the crystalline Si and of the SiH_4 and PH_3 molecules, and by evaluating the SiH_4 vibrational frequencies. Suitable periodicity conditions have been used in the molecular case. The computed Si—Si, Si—H and P—H bond lengths are 2.34, 1.523, and 1.460 Å, respectively, in good agreement with the experimental values (2.35 Å from Ref. 23, 1.481 and 1.420 Å from Ref. 24). The theoretical estimates for the silane stretching- and bending-mode frequencies (2000 and 800 cm^{-1}) are in satisfactory agreement with the experimental ones (2189 and 913 cm^{-1}),[25] and point toward an underestimate of the Si-H interaction. Further critical parameters are the supercell size, the number of special **k** points, and the kinetic-energy cutoff, which determines the basis-set size. The first parameter has been tested by using supercells of 8, 16, and 32 atoms to estimate the influence of the supercell size on the geometries and on the vibrational frequencies. The second one has been studied within the Monkhorst-Pack scheme[20] by using special-points sets equivalent to 2, 10 and 28 **k**-points in the bulk Si irreducible wedge of the Brillouin zone. The third one has been investigated by using kinetic-energy cutoffs ranging from 12 to 22 Ry. It has been found that reliable results can be obtained by using a 16-atom supercell, a set of special points equivalent to 10 Monkhorst-Pack **k** points, and an 18-Ry cutoff. In this case, the supercell contains 15 Si atoms, 1 P atom, and 1 H atom; the lattice is a fcc one whose lattice constant is twice that of bulk Si.

In order to find the H equilibrium positions, the high-symmetry sites shown in Fig. 1 have been investigated by using the Hellmann-Feynman[26] force-minimization scheme to fully relax the supercell geometry. This procedure results in a stable AB-Si site, in metastable AB-P and BC sites, and in unstable T, H, C, and M sites.[27] The bond-center site between two silicon atoms, BC*, has been found to be ≈ 0.5 eV higher in energy than the BC site and it has not been further investigated. Bond-length and atomic-displacement values for the stable and metastable sites of the H atom are reported in Table II, together with total-energy values. A rough estimate of the height of the energy barriers around the stable and the metastable sites has given values of $\simeq 0.4\pm0.1$ eV.

In the 16-atom supercell, the vibrational energies of the H local modes have been evaluated by the following procedures. The H atom has been moved away from its equilibrium position while keeping the atoms of the host crys-

TABLE II. Si-P-H complex geometries and vibrational energy values for the H atom located at different sites of the host lattice, as obtained in the present work. Atomic displacements from the unrelaxed positions are assumed to have a positive sign whenever the atom moves in the [111] direction from the P atom toward the Si one (see Fig. 1). The fourth and fifth lines give the values for the ir-absorption lines observed in hydrogenated Si:P and reported in Refs. 6 and 7, respectively.

Sites	ΔE (eV)	ΔP (Å)	ΔSi (Å)	H-Si (Å)	H-P (Å)	P-Si (Å)	$\tilde{\nu}_s$ (cm^{-1})	$\tilde{\nu}_b$ (cm^{-1})
AB-Si	0.00	0.14	0.52	1.65		2.72	1450	720
AB-P	0.54	−0.38	−0.16		1.59	2.56	1440	560
BC	1.09	−0.40	0.54	1.70	1.58	3.28	1515	980
AB-Si							1555	809
AB-Si							~2100	

tal frozen in the positions of the minimum-energy configuration. The force constants have been then estimated by fitting the total-energy values to a parabola, and, independently, by evaluating the Hellmann-Feynman restoring forces which act on the H atom. In both cases, the H displacements must be small enough to remain in the harmonicity region, yet large enough to overcome numerical noise. The accuracy of the above procedures has therefore been tested by a comparison with a phonon calculation in the 8-atom supercell. In both ways, values which agree within less than 10 cm^{-1} have been obtained. The average values for the stretching- and bending-mode energies are reported in Table II for the stable and the metastable H sites. The present PPDF picture for the H stable site closely matches that proposed in Ref. 6 on the grounds of an analysis of infrared-absorption spectra in hydrogenated n-type Si. Very good agreement[28] is indeed found between the frequency values obtained in the present work for the stable AB-Si site and the experimental ones. Moreover, H at the AB-Si site accounts well for the observation of a trigonal symmetry for the ir-absorption lines, of an almost complete independence on donor species of the energies of these absorption lines, and of donor passivation. The latter has been investigated through a comparison of the electronic density of states in hydrogenated Si:P with that in unhydrogenated Si:P. Passivation is positively achieved for H at the AB-Si site, while it is doubtful for the AB-P case and missing for the BC case, as will be discussed elsewhere in greater detail.

The HF results agree with the present PPDF ones except for the values of the stretching frequencies, which, however, have an experimental counterpart. The difference between the H-Si vibrational frequencies in the two methods can be related to a different description of the Si-P interaction, as shown by an inspection of Tables I and II. In fact, the P and Si atoms move away in opposite directions from their unrelaxed positions in all the HF calculations, and in the same direction in the PPDF treatments, giving rise to quite different Si—P bond lengths. This suggests a Si-P interaction still active in the PPDF picture, and nearly missing in the HF one, where the atomic character is likely to be excessive. This residual interaction results in a weakening of the H—Si bond and in a decrease for the corresponding vibrational frequency. Concerning the donor passivation, this is complete for H in the AB-P site, uncertain for H in the stable AB-Si site, and missing for H in the BC site in the HF treatment.[15] The atomic character shown by the HF picture is weakened in the PPDF picture, where a full passivation is achieved for H in the stable AB-Si site, in agreement with the electronic density-of-states analysis and the experimental evidence. However, both methods must result in the same geometry and H vibrational frequency values, provided the convergence of the results with respect to the critical parameters is thoroughly achieved and that correlation effects are negligible. On the PPDF side, the present results seem well established, although their slow convergence with supercell size may suggest further tests. This would require, however, exceedingly heavy computer resources. On the HF side, an increase of the basis set and of the finite cluster size seems advisable.[29] This, in fact, would increase the electronic delocalization, poorly handled in a HF approach,[15] thus resulting in a stronger Si-P interaction. The agreement between the stretching energy evaluated by the Hartree-Fock approach and that reported in Ref.7 would then be accidental.

Note added. After the original submission of this paper for publication, PPDF results virtually identical to those presented here have been published by two different groups.[30,31]

This work was supported in part by the Swiss National Science Foundation under Grant No 20-5446-87. It is a pleasure to thank S. de Gironcoli for helpful and stimulating discussions and W.B. Fowler for having provided us with results of his paper prior to publication.

---

[*] Permanent address: Istituto di Teoria e Struttura Elettronica (ITSE), Consiglio Nazionale delle Ricerche (CNR), Casella Postale 10, via Salaria Km. 29.5, I-00016 Monterotondo Scalo, Italy.

[1] S.J. Pearton, J.W. Corbett, and T.S. Shi, Appl. Phys. A **43**, 153 (1987), and references therein.

[2] J.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).

[3] C.-T. Sah, J.Y.-C. Sun, and J.J.-T. Tzou, Appl. Phys. Lett. **43**, 204 (1983).

[4] K. Bergman, M. Stavola, S.J. Pearton, and T. Hayes, Phys. Rev. B **38**, 9643 (1988).

[5] N.M. Johnson and C. Herring, Phys. Rev. B **38**, 1581 (1988).

[6] K. Bergman, M. Stavola, S.J. Pearton, and J. Lopata, Phys. Rev. B **37**, 2770 (1988).

[7] D. Tripathi, P.C. Srivastava, and S. Chandra, Phys. Rev. B **39**, 13 420 (1989).

[8] G.G. DeLeo and W.B. Fowler, in *Hydrogen in Semiconductors*, edited by J.I. Pankove and N.M. Johnson, Vol. X of *Semiconductors and Semimetals*, edited by R.K. Willardson and A.C. Beer (Academic, New York, in press), and references therein.

[9] N.M. Johnson, C. Herring, and D.J. Chadi, Phys. Rev. Lett. **56**, 769 (1988).

[10] P.J.H. Denteneer, C.G. Van de Walle, and S.T. Pantelides, Phys. Rev. B **39**, 10 809 (1989).

[11] P. Deak, L.C. Snyder, and J.C. Corbett, Phys. Rev. B **37**, 6887 (1988).

[12] S.K. Estreicher, L. Throckmorton, and D.S. Marynick, Phys. Rev. B **39**, 13 241 (1989).

[13] K.J. Chang and D.J. Chadi, Phys. Rev. Lett. **60**, 1422

(1988).

[14] A. Amore Bonapasta, A. Lapiccirella, N. Tomassini, and M. Capizzi, Phys. Rev. B **36**, 6228 (1987).

[15] A. Amore Bonapasta, A. Lapiccirella, N. Tomassini, and M. Capizzi, Phys. Rev. B **39**, 12 630 (1989).

[16] *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

[17] R.M. Martin, in *Electronic Structure, Dynamics and Quantum Structural Properties of Condensed Matter*, edited by J.T. Devreese and P. Van Camp (Plenum, New York, 1985).

[18] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[19] D.R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494(1979).

[20] A. Baldereschi, Phys. Rev. B **7**, 5212 (1973); D.J. Chadi and M.L. Cohen, *ibid.* **8**, 5747 (1973); H.J. Monkhorst and J.D. Pack, *ibid.* **13**, 5188 (1976).

[21] S. Baroni and R. Resta, Phys. Rev. B **33**, 7017 (1986).

[22] The parameter values for P are $Z_v = 5$, $r_{c0} = 0.98$, $r_0 = 0.82$, $a_0 = 9.524\,684$, $b_0 = -5.464\,465$, $r_1 = 0.88$, $a_1 = 2.745\,890$, $b_1 = -1.352\,263$, $r_2 = 0.88$, $a_2 = -5.607\,887$, and $b_2 = 1.277\,630$; those for H are $Z_v = 1$, $r_{c0} = 0.25$, $r_0 = 0.284$, $a_0 = -1.9287$, and $b_0 = 0.3374$.

[23] W. Parrish, Acta Crystallogr. **13**, 838 (1960).

[24] J.H. Callomon, E. Hirota, K. Kukitzu, D.J. Lafferty, E.G. Maki, and C.S. Pate, in *Structural Data on Free Polyatomic Molecules*, Vol. 7 of *Landolt-Börnstein, Functional Relationships in Science and Technology*, New Series, Gp. II, edited by K.H. Hellwege and A.M. Hellwege (Springer, Berlin, 1976).

[25] H.W. Kattenberg and A. Oskam, J. Mol. Spectrosc. **49**, 52 (1874).

[26] H. Hellmann, *Einführung in die Quantenchemie* (Deuticke, Leipzig, 1937); R.P. Feynman, Phys. Rev. **56**, 340 (1939).

[27] For the BC site, a residual dependence of the geometrical parameters on the supercell size has been still observed.

[28] The values for the stretching- and bending-mode energies reported in Table II are underestimated by a maximum of 100 cm^{-1}. In fact, the stretching energy for H in the AB-Si site progressively increases with the kinetic-energy cutoff and with the number of the special **k** points, the estimated convergence being within 100 cm^{-1}. Moreover, the PPDF method gives $\mathrm{SiH_4}$ vibrational frequency values roughly 10% lower than the experimental ones.

[29] The finite-cluster-size limitations could be overcome by using a HF method in a supercell approach (i.e., by applying periodic boundary conditions), if the resulting impurity interactions do not become the crucial problem.

[30] S. B. Zhang and D. J. Chadi, Phys. Rev. B **41**, 3882 (1990).

[31] P. J. H. Denteneer, C. G. Van de Walle, and S. T. Pantelides, Phys. Rev. B **41**, 3885 (1990).