RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 11 15 OCTOBER 1987-I

Hydrogen passivation of shallow acceptors in *c*-Si: An *ab initio* approach

A. Amore Bonapasta and A. Lapiccirella
Consiglio Nazionale delle Ricerche, Istituto di Teoria e Struttura Elettronica, Area della Ricerca di Roma,
Via Salaria, Km 29.5, CP 10, 00016 Monterotondo Scalo, Italy

N. Tomassini
Consiglio Nazionale delle Ricerche, Istituto di Metodologie Avanzate Inorganiche, Area della Ricerca di Roma,
Via Salaria, Km 29.5, CP 10, 00016 Monterotondo Scalo, Italy

M. Capizzi
Istituto di Fisica G. Marconi, Università degli Studi di Roma "La Sapienza," Piazzale le Aldo Moro 2,
00185 Roma, Italy

(Received 1 December 1987; revised manuscript received 23 June 1987)

Two different models have been recently discussed to explain the hydrogen passivation of shallow acceptors in *c*-Si without achieving a unified picture. In the present work, these two models are analyzed in a full *ab initio* Hartree-Fock cluster-molecular approach. It is shown that the on-line Si-H-B configuration is the most likely one. The ability of the hydrogen atom to form a three-center bond and the crucial role of relaxation effects on the geometrical structure are evinced.

The electrical deactivation of shallow acceptors observed in hydrogenated crystal silicon, the related far-infrared-absorption peak (FIR), and its isotopic shift have been the subject of increasing experimental and theoretical interest in the last few years.[1-6]

In particular, two theoretical models, founded on different silicon-hydrogen-boron atomic arrangements, have been investigated in a cluster-molecular approach. In the first one, suggested by Pankove, Zanzucchi, Magee, and Lucovsky[5] and hereafter referred to as Si-H-B, the hydrogen atom is located between the boron atom and the nearby silicon atom in the ⟨111⟩ direction, thus saturating the silicon dangling bond.[7,8] The equilibrium geometry of this model has been obtained by carrying out modified neglect of differential-overlap (MNDO)[9] total-energy computations, whereas the passivation mechanism has been discussed in the light of a multiple scattering (MS) $X\alpha$ (Ref. 10) orbital energy analysis. In the second model, suggested by Assali and Leite and hereafter referred to as H-B, the hydrogen atom is covalently bonded to the boron atom and is located along the line joining the tetrahedral interstitial site [Td in Fig. 1(a)] and the impurity site.[11] This model is based on the MS $X\alpha$ evaluation of both the minimum energy structure and the electronic energy levels.

A debate arose about these models which can both explain the passivation mechanism and quantitatively account for the FIR absorption data,[8,12,13] although they are based on quite different silicon-hydrogen-boron configurations. Therefore, an unambiguous identification of the hydrogen equilibrium position, which is a crucial point to understand the passivation mechanism, cannot be considered achieved yet.

On the other hand, it is widely recognized that good estimates of the atomic positions can be obtained by means of full *ab initio* total-energy calculations carried out on cluster-molecular models. In the present work, for the first time full *ab initio* methods have been used to investigate the H position problem quoted above. In particular, we have employed the *ab initio* HFR-MO-LCAO-SCF method (Hartree-Fock-Roothaan molecular-orbitals linear combination of atomic orbitals self-consistent field) to compute the total energy of a $Si_7H_{19}B$ cluster whose shape

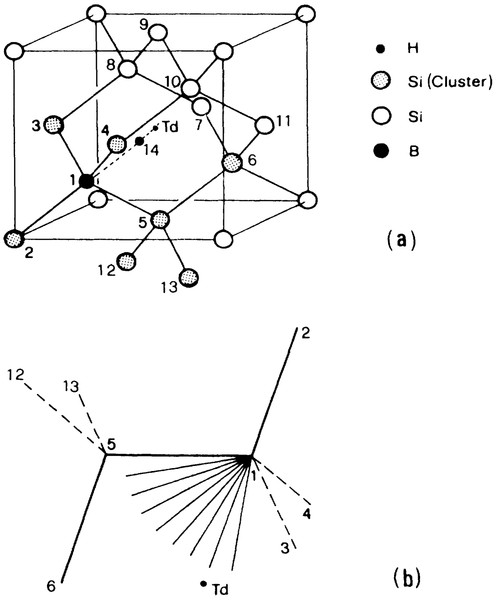

FIG. 1. (a) $Si_7H_{19}B$ cluster model partially surrounded by the *c*-Si lattice. The eighteen H atoms saturating the Si dangling bonds are not shown. (b) View of the radial lines used in the total-energy calculations discussed in the text.

is shown in Fig. 1(a) with the surrounding *c*-Si structure. The selected cluster assures a correct environment for the B, Si, and H atoms involved in the passivation mechanism [atoms 1, 5, and 14 in Fig. 1(a)]. Total-energy calculations of the larger $Si_{10}H_{19}B$ cluster [atoms 1 to 11 and 14 in Fig. 1(a)] show indeed, as will be discussed later, that a hydrogen atom located along the Td-B line moves toward the B atom (the Td site is not a stable one). Therefore, it is mainly influenced by the nearest-neighbor silicons (atoms 3, 4, and 5). Furthermore, the most significant Si and B atoms cited above (atoms 1 and 5) are both surrounded by their first neighbors

All calculations were carried out by means of the GAUSSIAN-80 program[14] and of the STO-3G basis set[15] whose reliability to predict correct geometries (bond angles and lengths) with a satisfactory degree of accuracy has been verified on a wide variety of small molecules.[16]

Detailed total-energy investigations have been performed in two steps: In the first one, a preliminary study of a large number of unrelaxed configurations gives indications about the more interesting regions of the potential energy surface; in the second one, relaxation effects are included on a restricted group of geometrical configurations selected on the grounds of the suggestions given by the previous step. The final picture of the potential surface has been obtained merging the results of both steps. Following this approach, a total-energy map has been obtained for the selected $Si_7H_{19}B$ cluster by moving the hydrogen atom along the radial lines shown in Fig. 1(b), while all the remaining atoms were kept fixed. The map is shown in Fig. 2, where the full radial lines identify the explored geometrical configurations and the Si-B line is at 0°.

The topological analysis of the resulting potential surface has been focused on three regions: the Td-B line region, the energy minimum region, and the Si-B line one.

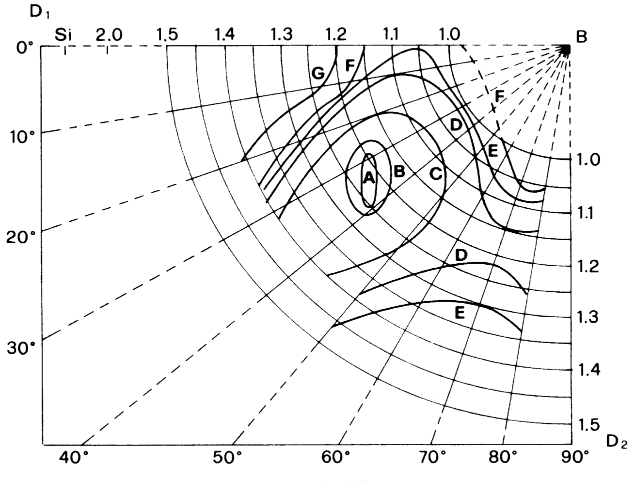

FIG. 2. Total-energy map of different $Si_7H_{19}B$ geometrical structures. Full radial segments show the H atom positions investigated in this work. The isoenergetic line labels, from *A* to *F*, correspond to increasing energy values. In the explored region, the length unit has been increased by a factor of 4.7. Distances from B atom (D_1 and D_2) are quoted in angstroms.

The H atom has no stable positions along the Td-B line which is located at 70.53°. However, a minimum is found on this line at 1.20 Å from the B atom, which corresponds to a total energy of −2034.4591 a.u. A saddle point is found on the radial line at 72° and at about 1.18 Å from the boron atom. Each point on this line—hereafter referred to as "saddle line"—gives a maximum for the energy values calculated along the transverse direction. The slight displacement between the saddle and the Td-B lines (1.47°) is due to the lack of some crystal symmetry elements in the present test geometry [i.e., two Td-site Si nearest neighbors, atoms 8 and 10 in Fig. 1(a)]. Therefore, the "real" saddle line is the Td-B itself. These two Si atoms missing in the $Si_7H_{19}B$ cluster have been included in the larger $Si_{10}H_{19}B$ cluster introduced above. Total-energy calculations performed on this cluster lead to the same conclusions for the Td-B line, whose properties, then, do not depend appreciably on this enlargement of the cluster size.

The absolute minimum is found roughly at 34° and at 1.22 Å from the boron atom, while the Si-H distance is 1.50 Å. The comparison of these values with the diborane B-H distance (1.21 Å) (Ref. 17) and the disilane Si-H one (1.49 Å) (Ref. 18) suggests a three-center bond configuration with the H atom outside the Si-B bond. The corresponding total-energy value is −2034.4854 a.u., i.e., 0.72 eV lower than the minimum on the Td-B line.

On the Si-B line the hydrogen atom has no stable positions and the energy values found along this line are higher than those found along the Td-B one.

As mentioned above, these calculations, done within a fixed geometrical environment, are only a first step in the analysis of the potential surface of the moving hydrogen: Relaxation geometry effects have to be taken into account in order to go beyond this approximation. Then, energy relaxation calculations based on the Fletcher and Powell (FP) energy minimization procedure[19] have been performed in a few selected points within the three regions quoted above. The Si, H, and B atoms have been kept fixed in the plane of the map shown in Fig. 2.

The three-center bond configuration found in the unrelaxed approach, the chemical properties of the hydrogen atom, and the Si-H-Si linear atomic arrangement investigated in hydrogenated amorphous silicon[20] suggest that this atom moves toward the Si-B line when relaxation effects are included. This line was therefore investigated by means of the FP procedure allowing the Si, H, and B atoms to move freely and independently along the line and keeping the remaining six silyl fragments ($-SiH_3$) fixed at the crystalline positions. The hydrogen atom was also allowed to bend out of the Si-B line. The optimization procedure has found a true minimum position along the Si-B line with a total energy equal to −2034.5747 a.u., 2.43 eV lower than the map minimum and 3.14 eV lower than the Td-B minimum found in the unrelaxed approximation. This minimum is located at a Si-H distance of 1.459 Å and at an H-B distance of 1.59 Å. This on-line Si-H-B configuration is quite similar to that found in Ref. 8. The shape and the H-B distance of this geometry, although different from those found in the unrelaxed case, are nevertheless consistent with a three-center interaction, as will be discussed later. The increase of the Si-B distance from the initial value of 2.35 to 3.049 Å is due to a small displacement of the Si atom and a larger one of the B atom. It must be noted that the insertion of the H atom in the Si-B line is favored by an intrinsic trend of the B atom to move away from the Si atom.

This drift is observed when the B atom is let free to move while the H atom is kept on the Td-B line (i.e., the Assali and Leite configuration). A cluster relaxation approach based on these constraints shows, indeed, that the B-H distance decreases from 1.18 to 1.15 Å and, more meaningfully, that the B-Si distance increases from 2.351 to 2.435 Å. The total energy of this configuration is −2034.4600 a.u., 3.12 eV higher than the absolute energy minimum found on the Si-B line.

The Td-B line has also been examined by allowing H and B atoms to move without constraints, but requiring the H atom to remain in the map plane. The FP procedure results show that the Td-B region still corresponds to a saddle situation.

Finally, the map region around the energy minimum position found in the unrelaxed configuration has been investigated. The initial Si and B coordinates were those determined in the relaxed case for the three centers on the Si-B line discussed above. The H ones, instead, were those found for the minimum in the unrelaxed case. It is found that the H atom is strongly pushed toward the Si-B line, leading to the disappearance of the unrelaxed minimum and confirming that the minimum found studying this line is the absolute one.

The on-line Si-H-B configuration shows appreciable three-center interactions suggested by a bond-order[21] analysis, even in the relaxed case. Bond orders estimate the interatomic electronic charge, i.e., they account for the chemical bonding. The H-B bond order is 0.07 a.u. for the relaxed minimum, about one-third of that found for the diboranelike unrelaxed geometry (0.19 a.u.), while the H—Si bond order is 0.26 a.u. (0.17 a.u. for the unrelaxed minimum): An H-B interaction therefore can be observed in addition to a stronger H-Si one. Analogous three-center interactions are suggested in Ref. 8 on the ground of a vibrational frequency analysis.

In summary, a model-cluster approach has been adopted to investigate the equilibrium structure problem related to the hydrogen passivation of shallow acceptors in *c*-Si. All calculations have been performed in this work for the first time in the framework of full *ab initio* methods. A total-energy map has been evaluated for the hydrogen atom moving in a fixed environment. A minimum has been found for the H atom sitting roughly in the center of the triangle formed by the B, the Td, and the nearest Si sites. The inclusion of relaxation effects moves the total-energy minimum in a new position between the Si and B atoms along the Si-B line, and deepens it by 2.43 eV with respect to the unrelaxed configuration. In both the relaxed and unrelaxed configurations, the Td-B line is a saddle line for clusters up to ten silicon atoms, once more confirming previous results.[7,8,12] The comparison between unrelaxed and relaxed geometries clearly points to the crucial role of relaxation effects when dealing with problems in which potential barriers are relevant. The agreement between De Leo and Fowler's results and present results suggests that the on-line Si-H-B model is the most likely one.

---

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

[2] C.-T. Sah, J. Y.-C. Sun, and J. J.-T. Tzou, J. Appl. Phys. **54**, 5864 (1983).

[3] J. I. Pankove, D. E. Carlson, J. E. Berkeyheiser, and R. O. Wance, Phys. Rev. Lett. **51**, 2224 (1983).

[4] W. L. Hansen, S. J. Pearton, and E. E. Haller, Appl. Phys. Lett. **44**, 606 (1984).

[5] J. I. Pankove, P. J. Zanzucchi, C. W. Magee, and G. Lucovsky, Appl. Phys. Lett. **46**, 421 (1985).

[6] N. M. Johnson, Phys. Rev. B **31**, 5525 (1985).

[7] G. G. De Leo and W. B. Fowler, J. Electron. Mater. **14**, 745 (1985).

[8] G. G. De Leo and W. B. Fowler, Phys. Rev. B **31**, 6861 (1985).

[9] M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc. **99**, 4899 (1977).

[10] K. H. Johnson and F. C. Smith, Jr., Phys. Rev. B **5**, 831 (1972).

[11] L. V. C. Assali and J. R. Leite, Phys. Rev. Lett. **55**, 980 (1985).

[12] G. G. De Leo and W. B. Fowler, Phys. Rev. Lett. **56**, 402 (1986).

[13] L. V. C. Assali and J. R. Leite, Phys. Rev. Lett. **56**, 403 (1986).

[14] J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. De Frees, H. B. Schlegel, S. Topiol, L. R. Kahan, and J. A. Pople in GAUSSIAN 80, Manual of QCEP Programs No. 406 and No. 437, Indiana University, Bloomington, IN, 1980.

[15] W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **52**, 2769 (1970).

[16] J. A. Pople, in *Application of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), p. 1.

[17] K. Kuchitsu, J. Chem. Phys. **49**, 4456 (1968).

[18] B. Beagley, A. R. Conrad, J. M. Freeman, J. J. Monaghan, B. G. Norton, and G. C. Holywell, J. Mol. Struct. **11**, 371 (1972).

[19] R. Fletcher and M. J. D. Powell, Comput. J. **6**, 163 (1963).

[20] R. Zacher, L. C. Allen, and D. C. Licciardello, J. Non-Cryst. Solids **85**, 13 (1986).

[21] R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).