RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 41, NUMBER 8 15 MARCH 1990-I

Copper, lithium, and hydrogen passivation of boron in *c*-Si

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(Received 2 October 1989)

The geometries and chemical structures of lithium- and copper-passivated substitutional B in crystalline Si are calculated and compared to the ones of hydrogen-passivated B. The calculations are done at the approximate *ab initio* and *ab initio* Hartree-Fock levels with various basis sets in several clusters. In contrast to H which bridges an acceptor-Si bond and forms a stronger bond with Si than with the acceptor, Li and Cu are at the antibonding site to the boron atom, and form Li—B and Cu—B bonds. Their wave functions overlap with several host atoms. The results show that copper is a viable candidate as the observed passivator *X*.

Among the many roles played by hydrogen in semiconductors,[1,2] one of the most often discussed is its ability to passivate a variety of shallow acceptors[3,4] and donors[5,6] in crystalline silicon and other hosts. The passivation of shallow acceptors has been (and still is) actively investigated experimentally and theoretically (see, e.g., Refs. 1, 2, and 7-9). Total-energy calculations[7,8,10-12] agree that in the case of H-passivated boron, the lowest-energy configuration is realized when H is near the bond-centered (BC) site. Hydrogen forms a strong bond with one of the four Si nearest neighbors (NN's) to the boron atom. The latter becomes threefold coordinated, while H saturates the dangling fourth Si bond. Similar equilibrium structures are obtained for H-passivated Al (Refs. 7 and 10) and Ga (Ref. 7). Various authors disagree on whether the absolute minimum of the potential-energy surface (PES) correspond to H exactly on or slightly off the trigonal axis, but the general consensus is that the PES is quite flat for small displacements of H perpendicular to that axis. A metastable configuration (about 1.6 eV above the BC one) with H antibonding (AB) to a Si atom nearest to the boron has been predicted.[7,13] The configuration where *H* is AB to the acceptor is a saddle point of the energy (at least if the acceptor is B, Al, or Ga), some 3.5 eV above the BC site.[7] A number of experimental data support the BC configuration as the lowest-energy one (see, e.g., Refs. 14-18).

Hydrogen is not the only interstitial which has the ability to passivate shallow acceptors. The formation of {Li,B} pairs was observed by infrared (IR) spectroscopy[19] as early as 1966, and detailed IR and Raman spectra have been obtained and are consistent with a trigonally symmetric complex.[20] More recently, the formation of {Li,In} pairs has been detected by the perturbed-angular-correlation (PAC) technique.[21-23] Finally, an ultrafast diffusing defect labeled *X* has been shown to passivate shallow acceptors in silicon as well.[22-25] This defect, introduced by chemomechanical polishing of *p*-type Si wafers, is believed[25] to be interstitial copper (the diffusing species being Cu^+), or at least to be associated with it. The *X*-acceptor complex is not stable at room temperature. The {Li,In} and {*X*,In} PAC frequencies are symmetric relative to the $\langle 111 \rangle$ axes of the crystal.[23] Except for the fact that pairing occurs and that the complexes have trigonal symmetry, nothing is known about the equilibrium structures, electronic configurations, or passivation mechanisms. Further, the identification of *X* as interstitial Cu has not been theoretically confirmed.

In this study, the PES's of Li- and Cu-passivated substitutional boron in *c*-Si are calculated at various levels of molecular-orbital theory in several clusters. The net charge of all the clusters is zero. It is assumed that a diffusing Li^+ or Cu^+ ion is attracted to B^-, and that the long-ranged Coulomb attraction is responsible for bringing Li or Cu close to the acceptor. The present calculations deal with the resulting interactions. The geometries are optimized for Li and Cu AB to B , AB to one of the Si atoms nearest to B, and bridging a B—Si bond. Even though the latter is a strongly bent bond, it will be referred to as the "BC site." These three configurations, and the two tetrahedral interstitial (*T*) sites on either side of the complex, do not exhaust the possible stationary points of the PES. They are, however, the most likely configurations which will result in passivation. Approximate geometries and electronic structures were first obtained in a small cluster (Li or Cu in B Si_7H_{18}) with the method of partial retention of diatomic differential overlap (PRDDO).[26-29] The results[30] were then used as an input for higher level geometry optimizations [*ab initio* Hartree-Fock with minimal and split-valence (6-31 G) basis sets] in the same cluster, and for PRDDO calculations in larger clusters: $LiBSi_{43}H_{42}$ and $CuBSi_{34}H_{36}$, which contain five and four host atom shells around the BC and the substitutional sites, respectively. In each case, only the positions of three atoms were optimized: Li (or Cu), B, and the Si atom on the same axis. Because of the large spatial extent of the Li and Cu valence orbitals, the calculations have been repeated with several values of the (Slater) orbital exponent. The results obtained with the various methods, exponents, and clusters are qualitatively the same, and quantitatively similar. However, the Li and Cu valence orbitals are very diffuse and significantly overlap with all the atoms in their immediate neighborhood. In the small cluster, this includes several of the surface hydrogen saturators.[31] In the larger clusters, these saturators are much further away from Li or Cu, which then overlap only with the acceptor and host Si atoms. As a result, when going from a small to a large cluster, quantitative changes are found in the equilibrium geometries, total-energy differences, and overlap populations. The largest effect occurs for Cu in the BC configuration. In $CuBSi_7H_{18}$, Cu moves much further away from the center of the B—Si bond than it does in $CuBSi_{34}H_{36}$. It is (currently) impossible to perform geometry optimizations at the *ab initio* level in clusters of that size, in particular since the symmetry drops to C_1 in the bent BC configuration. Therefore, the equilibrium geometries reported below are the ones obtained with PRDDO in $LiBSi_{43}H_{42}$ and $CuBSi_{34}H_{36}$. The discussions of electronic structures, however, rely on the *ab initio* as well as on the PRDDO results.

Even though H, Li, and Cu all have a single *s* electron in their outermost shell (the atomic structures are $1s^1$, $[He]2s^1$, and $[Ar]3d^{10}4s^1$, respectively), their chemical properties are quite different. In fact, in the configurations discussed below, Cu is more similar to Li than H is to any of them. Table I summarizes some of the basic features relevant to the present discussion. Because the valence orbitals of Li and Cu are much more diffuse than the 1*s* orbital of H, the bond lengths involving Li and Cu are very long. In particular, these atoms form straight bridged bonds only if sufficient room is available, which is not the case in the Si lattice. Further, many examples of chemical compounds with Li or Cu bound to four or more atoms are easily found in basic inorganic chemistry textbooks.[32] Even though individual bonds may be weak, such "cages" are quite stable.

Figure 1 shows the lowest-energy configurations of H-, Li-, and Cu-passivated boron in *c*-Si. In addition to the equilibrium bond lengths, the "degrees of bonding"[33] are given. This index, obtained from the density matrix, is a measure of the amount of covalent character in a particular bond. It is 0.00 for a purely ionic bond, 1.00 (2.00) for a perfect two- (four-) electron bond, etc. In Fig. 1, only degrees of bonding larger than 0.07 are shown. All correspond to bonding interactions. Note that degrees of bonding are not related to bond strengths, i.e., cannot be used to estimate vibrational frequencies. In the lowest-energy configuration, H is bound to two atoms (Si and B), Cu to four (B and its three NN's), and Li to seven [B, its three NN's, and the three Si atoms nearest to the tetrahedral interstitial (*T*) site shown]. A number of similarities between {Li,B} and {Cu,B} pairs are evident, as are the differences with the {H,B} pair. Hydrogen passivates boron by saturating a Si dangling bond and has little overlap with the boron atom itself, which is essentially threefold coordinated. On the other hand, in the presence of Li or Cu, boron is fivefold coordinated, and the passivation results from the formation of a Li—B or a Cu—B covalent bond. Further, lithium and copper are in a cage and overlap with several host atoms. It is known[34,35] that interstitial Li occupies the *T* site in the perfect Si lattice. In the presence of substitutional B, the nearest *T* site is not a minimum of the PES, and Li moves towards B as shown in Fig. 1. The same holds for Cu. It should be noted that

TABLE I. Comparison between various properties (Ref. 32) of atomic H, Li, and Cu, and of their bond with hydrogen.

	H	Li	Cu
Ionic radius (Å)	10^{-5}	0.60	0.93
Covalent radius (Å)	0.28	1.23	1.17
Ionization potential (eV)	13.6	5.4	7.7
Bond length with H (Å)	0.75	1.61	1.73
Bond strength with H (eV)	4.5	2.5	2.9

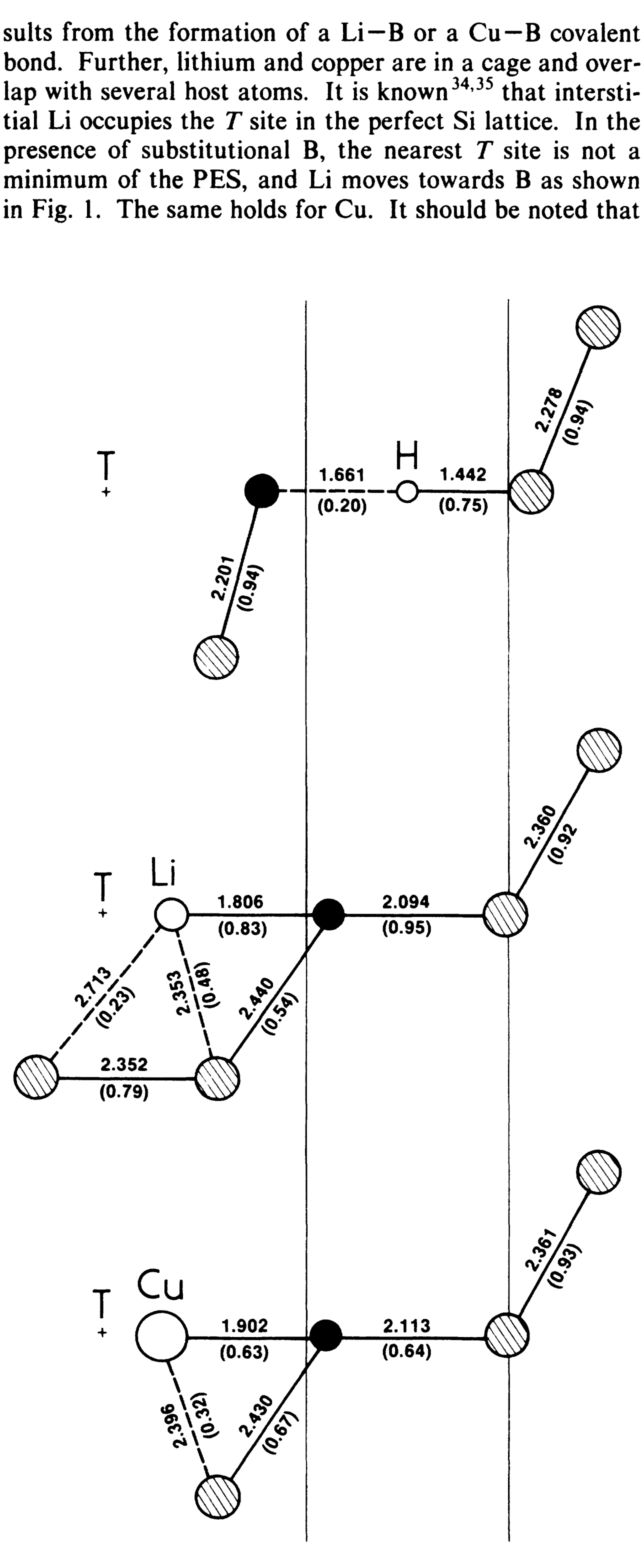

FIG. 1. Fraction of the {110} plane showing the lowest-energy configurations of the {H,B}, {Li,B}, and {Cu,B} pairs in *c*-Si. The thin vertical lines indicate the positions of the two substitutional sites in the perfect lattice. The bond lengths are in Å, and the "degrees of bonding" (Ref. 33) are given in parentheses (see text). Bonds amounting to less than 7% of a two-electron covalent bond are not drawn. The solid circle is the boron atom, the shaded circles are Si host atoms, and a tetrahedral interstitial site (*T*) is indicated.

the boron AB site for Li has been assumed[36] to fit theoretical vibrational spectra to IR absorption ones.[19] This site was also mentioned as the lowest-energy configuration for Li-passivated boron in a Comment by DeLeo and Fowler.[37]

The geometries have also been optimized for the following two configurations: Li or Cu at the BC site, and AB to a Si nearest to the boron atom. Because of the excessive amount of computing time required to perform gradient-based geometry optimizations in the large clusters used here, it was not possible to characterize with absolute certainty these stationary points as true local minima rather than saddle points of the PES. The arguments below are based on an analysis of the chemical structures involved and on the magnitude of total energy differences.

In the case of Cu, the second-lowest energy configuration is the BC site, 0.43 eV above the boron AB site. It is a strongly bent bond (the optimized B–Cu–Si bond angle is 92°), and the degrees of bonding are Cu–Si = 0.71, Cu–B = 0.58, *B*–Si = 0.35. Copper also forms bonds with three other host atoms: One of the boron NN (0.48) and two of the silicon NN's (0.11). In this configuration, a deep level appears above the top of the valence band (in the lowest-energy configuration, the gap after passivation is empty). The third sites for which geometry optimizations were performed corresponds to Cu at the AB site of a Si atom nearest to the boron. The energy for this site is 1.67 eV above the equilibrium configuration.

In the case of Li, the strongly bent BC site and the AB site to a Si atom are both much higher in energy than the configuration shown in Fig. 1 (1.8 and 2.1 eV, respectively). It is questionable whether either of these sites is a true minimum of the PES.

It should be noted here that the PAC data[23] consist of three signals for each of the {H,In}, {Li,In}, and {Cu,In} (or rather {*X*,In}) complexes. Each signal corresponds to a different electric field gradient, i.e., to a different charge distribution very near the complex. All nine PAC spectra have trigonal symmetry. However, these data do not imply that the observed complexes are metastable. The measured quantity is the angle between two γ rays. The first is emitted during the radioactive decay of ^{111}In into an excited state of ^{111}Cd. The second, emitted 0.12 μs later, corresponds to the transition to the ground state of ^{111}Cd. Thus, not only several electronic states are part of the process, but Cd (a double donor) is involved as well (for further discussion and a review, see Ref. 23). The present calculations show that only one stable configuration with ⟨111⟩ symmetry exists for the {Li,B} and {Cu,B} pairs.

In summary, the present calculations show that (a) passivation results from the formation of a covalent bond between Li or Cu and substitutional boron in *c*-Si, (b) Cu is a viable candidate as the passivator *X*, (c) the lowest-energy configuration corresponds to Li or Cu at the boron antibonding site, (d) after passivation, the B atom is fivefold coordinated and Li or Cu are in a cage, forming bonds with the acceptor and several host atoms, and (e) it is unlikely that metastable configurations with ⟨111⟩ symmetry exist.

The author owes thanks to Th. Wichert and J. Weber for stimulating discussions. This work was supported by the Robert A. Welch Foundation Grant No. D-1126. Most of the computing was done at the University of Texas Center of High Performance Computing in Austin (TX).

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