Properties of Hydrogen in Crystalline Silicon under Compression and Tension

C. S. Nichols,[(1)] D. R. Clarke,[(1)] and C. G. Van de Walle[(2)]

[(1)]*IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598*
[(2)]*Philips Research Laboratories, 345 Scarborough Road, Briarcliff Manor, New York 10510*
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Employing first-principles calculations, we have studied the behavior of hydrogen in crystalline silicon under compression and tension. The stable site for hydrogen is found to depend critically both on the pressure and on the hydrogen charge state. In particular, as the crystal is expanded, the energy of the bond-center site goes down with respect to the energy of the tetrahedral interstitial site. This result has implications for the behavior of hydrogen in the stress fields of dislocations, grain boundaries, and crack tips.

There is currently a great deal of interest concerning the electronic structure, equilibrium sites, diffusion, complexing, molecule formation, and dopant passivation properties of hydrogen (H) in crystalline silicon (c-Si). Experiment[1] and theoretical calculations[2] have furnished a comprehensive understanding of these properties under ambient pressures. However, little attention has been paid to the stable sites and electronic properties of H in c-Si (c-Si:H) under hydrostatic compression and tension. Such information is relevant for understanding the behavior of H in crystals which contain regions under compressive or tensile stress, such as around the core of dislocations and grain boundaries, as well as for understanding H solubility as a function of pressure.

In this Letter, we present the results of first-principles total-energy calculations exploring the behavior of H in c-Si as a function of its charge state, the Fermi-level position, and the lattice constant. We examine strains for which many physical properties are expected to vary linearly although no linearity is assumed *a priori*. For ambient pressures, our results are in accord with previously reported findings for the stable charge state, minimum-energy position, and energy difference between selected locations for the H atom.[2] However, under compression and tension, we find that the energy difference between the bond-center (BC) position and the tetrahedral (T) site changes rapidly, indicating a transition to a different minimum-energy position.

Our calculations are based on density-functional theory,[3] within the local-density approximation (LDA), and norm-conserving pseudopotentials[4] with a plane-wave basis. A momentum-space formalism is used to solve the relevant Schrödinger equation[5] for a supercell geometry.[6] *Ab initio* pseudopotentials, constructed according to the scheme of Hamann, Schlüter, and Chiang,[4] were used for the host Si atoms, while a Coulomb potential was used for the H atom. Careful convergence studies have been performed with respect to supercell size, plane-wave cutoff energy, and special-point sampling in the irreducible wedge of the Brillouin zone. In particular, it was necessary to use supercells of 32 atoms

such that the distance between H atoms in neighboring cells is 9.4 Å. Indeed, convergence of the final results could not be obtained with smaller cells under tension. Plane waves with a kinetic energy cutoff of 16 Ry were used in the expansions for the wave functions and potentials (plane waves up to 8 Ry were included in the exact diagonalization of the Hamiltonian while plane waves between 8 and 16 Ry were used in second-order Löwdin perturbation theory[7]). Convergence tests of the basis-set size show that for this particular basis, the energy differences are converged to less than 0.3 eV of the fully converged result. In addition, we have included symmetry-preserving relaxations of all first and second neighbors of the H atom in all the calculations. The different charge states of the H are treated following Van de Walle *et al.*[8] Spin polarization effects have not been included because such effects are small.[8]

Before investigating the properties of H in c-Si under compression and tension, both the bulk properties of c-Si and the previously reported results for c-Si:H under ambient pressure were reproduced. The total energy of the pure c-Si supercell was calculated at five different lattice constants (5.13, 5.28, 5.43, 5.58, and 5.73 Å), representing maximum strains of $\mp 5.5\%$. These particular values were chosen so as to avoid lattice constants corresponding to "jumps" in the energy versus volume curve[9] which arise because of discrete changes in the size of the basis set as the lattice constant is varied. All calculations were performed at a constant plane-wave cutoff and the results were fitted with a Murnaghan equation of state[10] to determine the equilibrium lattice constant, a_0, and the bulk modulus, B_0 (Table I). The agreement with the corresponding experimental properties is quite good for the lattice constant (-0.5% deviation from experiment) and, as is well known for such LDA calculations, somewhat poorer for the bulk modulus (-6% deviation from experiment).

We next introduced a single H atom into the host matrix at two representative sites. From previous studies,[2] it was determined that the global minimum, at the equilibrium lattice constant, is at the BC site (positive and

TABLE I. Tabulation of the calculated bulk moduli, B_0, and lattice constants, a_0, for the various charge states and positions of the H solute. The experimental values for pure crystalline Si are also included.

System	B_0 (GPa)	a_0 (Å)
Expt.	99.0	5.429
c-Si	93.0	5.404
H^0(BC)	88.9	5.427
H^0(T)	90.6	5.405
H^+(BC)	92.5	5.401
H^+(T)	94.3	5.377
H^-(BC)	85.8	5.453
H^-(T)	87.2	5.431

FIG. 1. Total-energy difference between H at the T and BC sites as a function of lattice constant for H in its different charge states.

neutral charge states) or at the T site (negative charge state). Following that work, the present study concentrates on these same two sites.

The total energy of H in the positive, neutral, and negative charge states at the two sites was calculated for the same five lattice constants used in the bulk Si calculation. Equilibrium lattice constants and bulk moduli were obtained from a fit with a Murnaghan equation and the results are also reproduced in Table I. For all the configurations studied, a softening (a decrease in the bulk modulus) is observed. The electronic structure of c-Si:H varies strongly as a function of the lattice constant. In the case at hand, we focus on the change with pressure in the energy difference between the H-induced level and the top of the valence band. For H at the T site, the defect level is slightly below the top of the valence-band maximum at ambient pressure in the negative charge state. In all charge states, the level shifts to lower energy at the rate of 1.5 eV/Å for increasing lattice constant.[11] For H at the BC site, the H-induced level is in the upper part of the band gap and shifts to lower energy at the rate of 0.4 eV/10Å for increasing lattice constant.

For each given charge state, a plot of the total-energy difference between hydrogen at the T site and at the BC site as a function of lattice constant was calculated. These curves are reproduced in Fig. 1. The total-energy difference is nearly linear with a negative slope over the entire range of strains investigated ($\mp 5.5\%$). This linear dependence arises because of the similarities of the bulk moduli calculated for H at the two different sites. Figure 1 indicates that under large enough *compression*, the T site is energetically preferred, while the negative slope of the total-energy difference indicates that the BC site becomes more favored under smaller compression or under *tension*. (For H^+, extrapolation of the calculations to slightly smaller lattice constants is required before this transition is observed.) Using the calculated bulk moduli and the lattice constant at which the crossover occurs, we can determine an upper limit for the pressure region in which the ambient-pressure global energy minimum can remain stable. These upper limits are
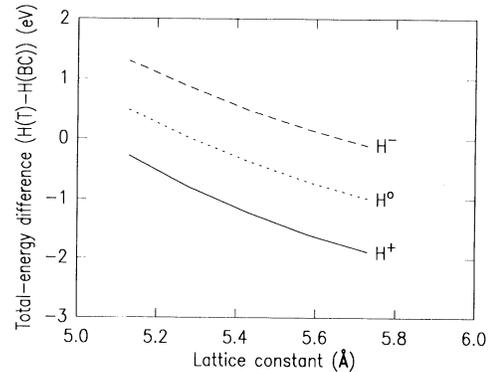
19.7 GPa (positive charge state), -12.0 GPa (negative charge state), and 6.9 GPa (neutral charge state), where we use the convention that positive pressure corresponds to compression, and negative pressure corresponds to tension. It should be noted that the extrapolated value for the positive charge state lies at a pressure which is beyond the phase transition from the diamond to the β-tin structure. These pressures are not modest but are accessible in some laboratories. (The case of tension is discussed below.)

These observations are intuitively reasonable and arise from the competition between two effects: size and electronic structure. For the smallest lattice constant studied (5.13 Å), the Si-H distance for H at the T site is 2.22 Å, while the Si-H distance for H at the BC site was calculated to be 1.52 Å. The latter value is subtantially reduced from the value 1.63 Å for H^0 at ambient pressure, indicating the more severe constraints imposed on the H solute by the surrounding lattice at the BC site. The T site poses less severe spatial constraints, explaining in part why it becomes increasingly favorable with respect to the BC site under pressure.

The effects of electronic structure on the transition from the T to the BC site are most conveniently demonstrated by defining a heat of solution for the single H concentration (3%) of interest in the present study:

$$E_{soln} \equiv E(H) - E_{bulk} - E_{atom}, \qquad (1)$$

where $E(H)$ is the total energy per supercell containing an H atom ($N+1$ atoms), E_{bulk} is the total energy of a bulk crystalline Si supercell (N atoms), and E_{atom} is the total energy of an isolated H pseudoatom. Because the total energy of the pseudoatom is a constant for each H atom location *inside* the crystal, an effective heat of solution may be defined as

$$E_{soln}^{eff} \equiv E_{soln} + E_{atom}. \qquad (1a)$$

The heats of solution defined in Eqs. (1) and (1a) are
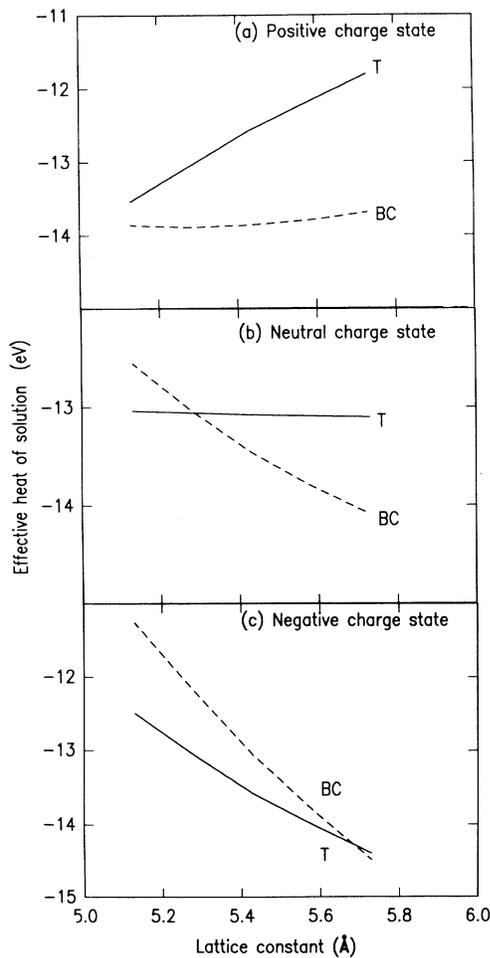
FIG. 2. Effective heat of solution of H at the T site (solid line) and at the BC site (dashed line).

valid for neutral species. For singly charged species, the heat of solution depends linearly on the Fermi-level position.[8] Note that the effective heat of solution defined in Eq. (1a) is negative and that the more negative it is, the greater the H solubility.

The effective heats of solution for H at the T site (solid line) and at the BC site (dashed line) for the positive, neutral, and negative charge states are plotted in Figs. 2(a)–2(c), respectively. Different charge states are obtained by taking or removing electrons to or from the Fermi level. For Figs. 2(a) and 2(c), it has been assumed that the Fermi level is at the bottom of the forbidden energy gap, making the material p-like. The n-type material is simulated by placing the Fermi level at the top of the *calculated* energy gap (0.6 eV). Thus, the heat of solution for the positive charge state in the n-type material is obtained by *adding* the calculated band gap to the p-type material value, while that for the negative charge state is obtained by *subtracting* the calculated band gap. Note that the heats of solution for the neutral

charge state are independent of the Fermi-level position. The different pressure dependences of the two heats of solution can be traced to differences in the electronic structure induced by H at the two locations.

H at the BC site interacts strongly with the two neighboring Si atoms and produces three levels.[12] The lowest energy level is completely bonding in nature and lies in the bulk of the valence band. There is also a corresponding antibonding level which lies in the conduction band. The third level has been identified as nonbonding by examining its charge density; it is this level which lies in the forbidden gap. On the other hand, for H at the T site, there is only a weak overlap with the neighboring Si atoms; a hydrogen-induced level is identified below the valence-band edge.

For positively charged H, it is clearly more favorable to produce the BC bonding level, which is fully occupied, and to leave the nonbonding level empty. This conclusion is valid for all strains investigated and is consistent with the heats of solution plotted in Fig. 2(a). For neutral H, the nonbonding level contains one electron, but its occupation is still favorable. However, the BC site energy rises rapidly as a function of pressure, and ultimately this site will become unstable. Finally, for negatively charged H, the BC nonbonding level must accommodate two electrons which imposes too high an energy cost and hence the T site is preferred. Additionally, because the T-site level drops in energy for larger lattice constants, as discussed above, it becomes increasingly favorable to occupy this level.

The calculated heats of solution also provide an understanding of the solubility of H in c-Si under various conditions. For p-type material, H is stable in the positive charge state (H^+). This can be seen by a direct comparison of Figs. 2(a)–2(c). For ambient pressure and under compression, H^+ is stable at the BC site. Application of hydrostatic pressure to p-type c-Si:H should have little effect on the H solubility because the BC heat of solution in Fig. 2(a) is relatively insensitive to pressure. On the other hand, for n-type material, H is stable in the negative charge state (H^-). Thus, for ambient pressure and under compression, H^- is stable at the T site. For increasing pressure, H^- becomes less soluble in the crystal because of the decreasing magnitude of the heat of solution, Fig. 2(c). H in c-Si is believed to be a negative-U system[1,8] so that the neutral charge state is never stable for any position of the Fermi level. This conclusion is indeed borne out by our results not only at ambient pressure but also under compression and tension. However, comparisons between different charge states are subject to larger error bars to the extent that they are limited by the LDA uncertainty. To the best of our knowledge, experimental data relevant to our theoretical finds regarding H solubility under pressure are lacking.

Application of hydrostatic compression is easily achieved by external means in diamond-anvil cells.

Crystalline regions under *tension* may be realized in samples which contain extended defects such as, for example, dislocations, grain boundaries (which may be envisioned as arrays of dislocation cores), and cracks. Consider first an isolated dislocation. In p-type Si, H^+ is stable at the BC site and the heat of solution depends only weakly on strain [Fig. 2(a)]. In n-type Si, H^- is stable at the T site for tensile strains up to $\approx 4\%$ but at the BC site for larger strains. The magnitude of the heat of solution for H^- is a strongly increasing function of lattice parameter, Fig. 2(c). From these findings, we predict that H in n-type Si will prefer the tensile strain field in the vicinity of a dislocation core over unstrained crystalline regions with the concomitant formation of a Cottrell atmosphere around the dislocation. No such effect is expected in p-type Si. There is also the possibility, not calculated here, of charge transfer between the H solute and the bonds at the dislocation core that could lead to compensation of the charge levels and also a difference in dislocation mobility under shear stress (akin to the Patel effect).

There exists a wealth of experimental data[13] concerning H passivation of grain boundaries in polycrystalline Si. Although the microscopic mechanism of such passivation is not clear and it is not known whether dopants are involved, we predict from the considerations of the previous paragraph that H will passivate grain boundaries in n-type Si more effectively than in p-type Si.

Finally, our findings may well have some relevance to the fracture of silicon in the presence of hydrogen. In the vicinity of a crack tip there is a volume of material under tensile stress, the value of which decreases as $1/\sqrt{r}$ away from the crack tip. In p-type Si, we would therefore expect that H^+ would preferably adopt a BC position in a region about the crack tip, possibly affecting the energy of cleavage and thereby altering the fracture resistance. Since in n-type Si, H remains in an interstitial position independent of pressure, no such effect is expected. We thus conjecture that p-type and n-type Si should exhibit a difference in fracture resistance, and if the rate of hydrogen diffusion to the tip region is kinetically limited, a difference in crack propagation rate at a given, constant driving force. Little experimental data appear to exist. An investigation of the fracture resistance of n-type Si in the presence of hydrogen has shown no difference from that in the absence of hydrogen.[14] The fracture resistance of p-type silicon in hydrogen does not appear to have yet been performed, although there are occasional cryptic remarks in the literature regarding the greater "brittleness" of p-type Si in the presence of hydrogen.[1,15]

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