PHYSICAL REVIEW B VOLUME 45, NUMBER 7 15 FEBRUARY 1992-I

Bonding of hydrogen to weak Si-Si bonds

Eugen Tarnow and R. A. Street
Xerox Palo Alto Research Center, Palo Alto, California 94304

(Received 16 September 1991)

Results of an *ab initio* investigation of the bonding of hydrogen to strained silicon-silicon bonds are reported. In particular, the effect of a bond-angle distortion is studied by introducing a lateral displacement of atomic planes in a supercell configuration. Compared to the normal bond-centered site, the hydrogen binding energy increases with strain by up to 1.5 eV and the hydrogen favors an asymmetrical site. The results are related to the bonding of hydrogen in amorphous silicon.

I. INTRODUCTION

The introduction of hydrogen into crystalline silicon results in several phenomena, including the passivation of dopants and defects, and the formation of clustered hydrogen structures.[1] In hydrogenated amorphous silicon, the hydrogen serves to eliminate most of the silicon dangling-bond defects, and is also implicated in the structural metastability effects.[2] The lowerest-energy state of a single neutral or positive hydrogen atom in a perfect Si crystal is the bond-center site, which lies about 1 eV below the vacuum level.[3] Bonded hydrogen configurations of up to about 2 eV lower energy than the bond-centered site exist at defects and impurity sites, and there are also hydrogen clusters of low energy. Most of the hydrogen in *a*-Si:H is tightly bound to single silicon atoms, either in isolation or in clusters. Hydrogen diffusion is explained by thermal excitation from the Si-H bonds into the higher-energy states, such as the bond-center sites.[1] However, the disorder of the amorphous-silicon network introduces a variety of Si-Si bond configurations. Measurements of the radial distribution function show that the distribution of bond lengths is quite narrow, but the rms bond-angle deviation is about 10°.[4] Strain in the Si-Si bond affects the energy of the hydrogen bond-center site and therefore may modify the diffusion energy.

Strained or weak Si-Si bonds also feature in models of defect creation and metastability in *a*-Si:H.[5] Defect creation by Si-Si bond breaking is expected to occur at the weakest bonds because the defect-formation energy is lowest. It has further been proposed that the broken bond is stabilized through attachment of hydrogen by a reaction of the type[6]

$$\mathrm{H}+(\text{Si-Si})_S \leftrightarrows \mathrm{SiH}\cdot\mathrm{Si}\ , \tag{1}$$

where $\cdot$Si and $(\text{Si-Si})_S$ represent a dangling bond and a strained bond, respectively. This model is based on the supposition that hydrogen binds more strongly to a strained Si-Si bond than to a normal bond, and that the H site is increasingly asymmetrical as the distortion of the bond is increased.

The effects of bond strain on the hydrogen bonding energy is therefore of interest to studies of both the hydrogen diffusion and defect metastability in *a*-Si:H. This paper describes calculations of the H bonding energies in distorted bonds. Our studies particularly focus on the effects of bond-angle strain, rather than distortions along the bond length, because this is the dominant form of strain in amorphous silicon. Some previous calculations have been made of hydrogen in strained bonds, using a computer-generated amorphous-silicon model.[7] We use a crystalline model, which allows an arbitrary choice of strain. The calculations are described in Sec. II, and are followed by the results in Sec. III, and a discussion of their application to the structure of *a*-Si:H in Sec. IV.

II. CALCULATIONS

The calculational details were as follows: The computations were performed within the framework of density-functional theory using the local-density approximation combined with pseudopotentials and the supercell method.[8] In all calculations a 32-atom supercell was used; one special **k** point $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ was used in the irreducible Brillouin zone. The plane-wave cutoff used was 7 Ry. Results of convergence tests are reported below.

The shear strain was introduced into the unit cell using the following method (see Fig. 1). One particular bond in

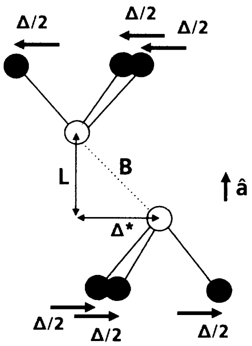


FIG. 1. Illustration of the configuration used to introduce strain. The solid circles indicate Si atoms moved to induce strain, and the open circles indicate the resulting "strained" Si atoms with a strained bond *B*. The displacement is parametrized in Δ. **â** indicates the original direction of bond *B*. Δ* indicates the lateral distance between the two strained Si atoms (perpendicular to **â**), and *L* indicates the longitudinal distance (parallel to **â**).

the unit cell is labeled *B*, and is defined by two atoms, each of which have three backbonding atoms. We imposed a transverse strain by moving these backbonding atoms transverse to the $\hat{a}$ direction, which is the original orientation of bond *B*. This movement was frozen into the backbonding atoms, which were then not allowed to relax. All other Si atoms in the unit cell were allowed to relax. The imposed strain was parametrized in the variable Δ, the relative displacement of the two sets of backbonding atoms. Notice that we can impose the displacement in both the positive and negative directions (the positive direction is defined by the arrows in Fig. 1). The two directions are equivalent only for infinitesimal displacements Δ. This can be most easily seen by considering that, for positive Δ, the bond *B* tends to line up with one backbond in each direction, while for negative Δ it tends to line up with *two* backbonds in either direction. In this work we concentrate on the positive direction, but also report one value from the negative direction. Due to the relaxation, the atoms forming bond *B* may have a smaller lateral displacement, which we denote Δ^*; the longitudinal distance is denoted *L*.

The H atom was placed in one of two positions: the symmetric position [Fig. 2(a)] or the asymmetric position [Fig. 2(b)]. The H atom cannot relax in the former position (the forces are 0 by symmetry), but is allowed to relax fully from the latter.

Due to the supercell approximation, there are secondary regions of strain, halfway between bond *B* of one supercell and bond *B* of the next supercell in the $\hat{a}$ direction. The effect of this strain is approximately canceled out in the calculations of the energy differences with and without the hydrogen, since both configurations are very similar in this region.

Three calculations were performed. Total energy and electronic states as a function of the stress: (i) without H, (ii) with H in the symmetric position, and (iii) with H in the asymmetric position. The charge of the unit cell in these calculations was 0, 1+, and 1+, respectively. One calculation is also reported for a neutral H configuration.

As a test of convergence, we studied the total energies of four different configurations: a Si-Si bond with and without an imposed Δ of 1.06 Å, and with and without an asymmetric H atom. We studied the properties of the total energy and first- and second-order energy differences. A first-order energy difference is, for example, the difference in energy between two configurations of different Δ, but with the same number of atoms in the cell. Our second-order energy difference is the difference between two first-order energy differences: one of a configuration with a H atom and another of a configuration without a H atom. We found that increasing the number of **k** points to eight changed the total energy by 0.7 eV, the first-order differences by 0.32 eV (out of 4.0 eV), and the second-order differences by 0.00 eV (out of 0.29 eV). In this paper we will consider only second-order energy differences. Increasing the energy cutoff from 7 to 9 Ry changed the first-order energy differences by 0.24 eV and the second-order energy differences by 0.02 eV. Tests up to 11 Ry were performed with these four configurations in a small eight-atom cell. We found that the energy changes upon going from 9 to 13 Ry were even smaller as compared with those from 7 to 9 Ry.[9]

III. RESULTS

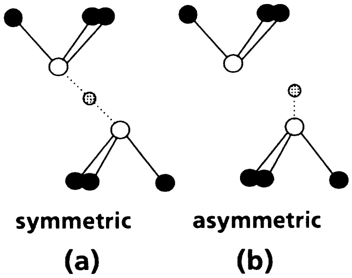
A. H strain-energy reduction

Let us consider the change in strain energy due to migration of the H atom to the strained Si-Si bond:

$$(\text{Si-H-Si})_N+(\text{Si-Si})_S\rightarrow(\text{Si-H-Si})_S+(\text{Si-Si})_N \ , \qquad (2)$$

where *N* and *S* represent normal and strained bonds, respectively. This is a general model for the particular reaction in Eq. (1). The resulting energy change for Eq. (2) is shown in Fig. 3. For both the symmetric (results always indicated with solid *circles*) and asymmetric (results always indicated with solid *triangles*) configurations, there is energy gained when the H atom is transferred from a normal bond to a strained bond. The energy is about 0.4 eV for a Δ of 1 Å. We also find that the asymmetric site is more favorable than the symmetric site. The energy difference between the two is 0.1 eV for a Δ of 1 Å, increasing to about 0.7 eV at $\Delta=2$ Å.

The H-induced strain-energy reduction changes the response of the atomic configurations. Figure 4 compares the lateral distance, Δ^*, over which the strained Si atoms


symmetric (a)

asymmetric (b)

FIG. 2. Placement of the H atoms (shaded circles) introduced at bond center. (a) Symmetric site; (b) asymmetric site. Note that the calculations relax H at the asymmetrical site to its lowest-energy state.

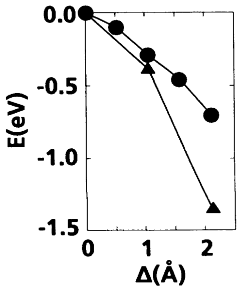


FIG. 3. Energy gained in the reaction described in Eq. (2). Triangles denote the asymmetric configuration and circles the symmetric configuration.

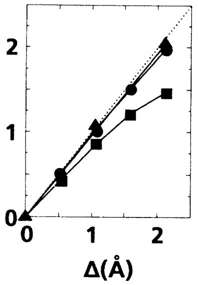


FIG. 4. Lateral distance Δ^* (see Fig. 1) of the strained Si atoms as a function of imposed displacement Δ. Squares denote distances from the configuration without H, circles distances from the symmetric configuration, and triangles distance from the asymmetric configuration.

move (vertical axis) with the lateral distance Δ imposed on the backbonded Si atoms (horizontal axis). The actual distance moved would be linear in the imposed distance if the material can easily accommodate the imposed stress, and we expect an increasing deviation from linearity, $\Delta-\Delta^*$, as the strain builds up. Figure 4 shows that in the presence of a H atom the imposed and actual distances are very close, with the asymmetric being the closest. In the absence of H (these results are always indicated with solid *squares*) there is a significant deviation.

We also examined the actual *longitudinal* distance L moved as a function of Δ. The result is presented in Fig. 5. The configurations with H start out at as bond-centered sites, for which the distance L is initially about 3.2 Å. We see that the change in longitudinal distance is linear for the asymmetrically placed H atom. The distance decreases to release the stress imposed by including the bond-centered H. This change in position is about 0.2 Å for a Δ of 1 Å. Symmetry imposes that the change is quadratic for either symmetrically placed H or no H at all. We note that the symmetrically placed H is not able to release the longitudinal strain as well as the asymmetrical configuration.

An unexpected finding is that the configuration without H also contracts longitudinally. Initially this is due to the tendency of the material to keep the bond between the central Si atoms. However, as Δ increases, this bond is retained as a result of the configuration losing the bonds to its backbonding atoms. The configuration we arrive at is shown in Fig. 6. The bond lengths of the central Si-Si bond B and the backbonds C are 2.29 and 2.76 Å, respectively.

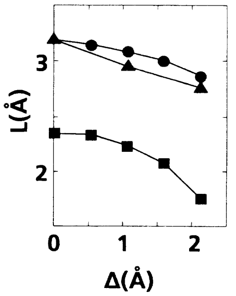


FIG. 5. Longitudinal distance L (see Fig. 1) of the strained Si atoms as a function of imposed displacement Δ. Squares denote distances from the configuration without H, circles distances from the symmetric configuration, and triangles from the asymmetric configuration.

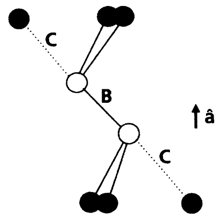


FIG. 6. Resulting bonding configuration for $\Delta=2.12$ Å. Notice that the longest bonds are the backbonds C (2.76 Å), not the strained bond B (2.29 Å).

Figure 7 shows the interplay between the bond lengths of the strained bond and the backbond (which is less strained). They both get somewhat elongated as the strain Δ is increased, but the backbond elongates more quickly. Between $\Delta=1.5$ and 2 Å the backbond has become so long that it starts to break. At this point the backbonding atom is becoming increasingly sp^2 hybridized to the atoms it remains bonded to. Indeed, it is now only 0.35 Å outside the plane created by its remaining bonded atoms (rather than 0.78 Å for an sp^3-hybridized atom). At the same time the central bond B starts to shorten.

This peculiar bond breaking is a result of the large stress induced in the *positive* Δ direction, which drives the backbonding atom into an sp^2-hybridized state. The opposite is true for the negative Δ direction, where we expect bond B to elongate while the two C bonds remain close to their bulk values. One calculation was performed for $\Delta=-1.06$ Å with the H in the nonsymmetric position. Here we found that the energy gain for transferring a H atom to the strained bond was smaller than that for the positive Δ direction (0.23 eV as compared to 0.39 eV for $\Delta=+1.06$ Å). We found that the backbond C was indeed shorter than the strained bond B (2.28 Å as compared to 2.44 Å). Thus it is apparent that the weak bond and "strained" bond can be different and the details of the strain and relaxation are sensitive to the specific local bonding configuration.

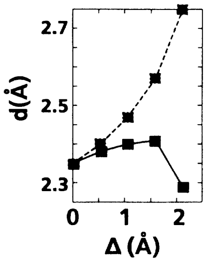


FIG. 7. Bond lengths d of the backbonds C (dashed line) and strain bond B (solid line; see Fig. 6).

B. Barrier of the two-state system associated with the H atom

Next we describe one property of the asymmetric position of the H atom, namely, the barrier for it to move from one Si to the other semiequivalent Si atom (the "semiequivalent" Si atom differs by a small relaxation due to the asymmetric position of the H atom). This barrier is displayed in Fig. 8 and was calculated for $\Delta = 2.12$ Å. The H is much lighter than the Si atoms, and accordingly the barrier was constructed by relaxing only the H position, keeping the Si atoms fixed. The horizontal coordinate in Fig. 8 labels the movement perpendicular to the $\hat{\mathbf{a}}$ axis. The barrier height is calculated to be about 0.6 eV, and the initial and final states differ in energy by about 0.2 eV. The latter energy difference is due to the fact that the Si lattice is not properly relaxed to optimize the energy at the second H position. This is a real dynamical effect.

C. Strain-energy relief from other impurities

A calculation was made to find out what other impurities would do to relieve bond strain energy. First we consider substitutional P. A configuration with $\Delta = 1.59$ Å was chosen, in which one of the two strained Si atoms was replaced by the P atom (in a singly positive charge state). No H atom was added. The configurations were allowed to relax and the calculated strain-energy difference with and without P was within 0.05 eV, compared to the corresponding H strain-relieving energy of about 0.70 eV. The general substitutional impurity can vary from being Si-like to being vacancylike, depending on its position in the Periodic Table. For example, while impurity-Si force constants for impurities close by (i.e., P) are nearly as large as the Si-Si force constants, the force constants for impurities far to the right or to the left in the Periodic Table can be as small as 30% of the Si-Si force constants.[10] Thus, to include predictions for the whole range of substitutional elements, a final calculation was undertaken in which one of the two strained Si atoms was removed to give the stress-relieving effect of the other extreme—the Si vacancy (here we used the doubly positive charge state). This gave a much larger effect, with an energy lowering of about 1.4 eV at $\Delta = 1.59$ Å, which is twice as strong as that of the bond-centered H atom. This result illustrates that hydrogen relieves about half of the strain at this value of Δ, since the vacancy provides almost complete strain relief of the distorted Si-Si bond.

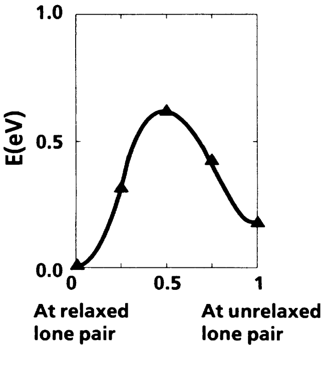


FIG. 8. Calculated energy barrier moving a proton from one strained Si atom to the other. Δ is 2.12 Å.

D. Electronic states of the strained configurations

The electronic states of the supercell at the $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ $\mathbf{k}$ point are shown in Fig. 9 as a function of the induced strain. The thick horizontal lines represent the calculated top of the valence band and the bottom of the conduction band of pure Si. Solid lines indicate filled states, dashed lines indicate empty states. Squares denote states from the configuration without H, circles states from the symmetric configuration, and triangles states from the asymmetric configuration. We see that in the absence of H there are two bands, one below the top of the valence band and one above the bottom of the conduction band, that move into the gap as the strain is increased. They both start away from the gap, due to the artificially large gap at the special $\mathbf{k}$ point considered. Both the highest filled state and the lowest empty states for $\Delta = 1.06$ Å are delocalized with only about 7% centered around any one atom.

As strain is increased, in the presence of H, the states in the top of the valence band closely follow the state for the configuration without the H (see Fig. 9). However, the states near the conduction band are more sensitive. For zero stress, the H-induced state is in the gap; it is the empty antibonding state of the bond-centered H configuration.[11] It consists of two lobes from either Si atoms with a node at the H atom. Notice also that the symmetric and asymmetric configurations are initially similar, but they differ as the stress is increased. The asymmetric state changes the least; its energy comes down slowly and intersects the condution-band state for the system without H. The symmetric states changes more quickly and does not intersect the conduction-band state. In the $\Delta = 1.06$ Å configuration, neither highest-filled state is localized (less than about 6% on either atom). The lowest unfilled state is considerably localized.

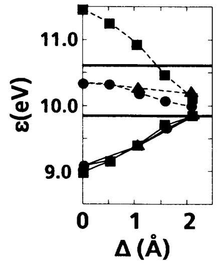


FIG. 9. Electronic states in the vicinity of the gap as a function of imposed stress Δ. Solid lines indicate filled states; dashed lines indicate empty states. The thick horizontal lines mark the top of the valence band (at about 9.8 eV) and the bottom of the conduction band (at about 10.6 eV) of the present calculation. Squares denote states from the configuration without H, circles states from the symmetric configuration, and triangles state from the asymmetric configuration.

For the symmetric configuration, this has about 26% of the charge on the H atom and 22% on each of the two nearest-neighboring Si atoms. As we increase the strain, the lowest unfilled state starts to disperse. Let us consider an interval of 2 eV around the center of the gap and study the projection on a p_z state (where the z direction coincides with the $\hat{a}$ axis of Fig. 1). Here we find that the charge density on the Si atom closest to the H decreases (20%, 15%, and 10% for $\Delta=0$, 1.06, and 2.12 Å, respectively), because a Si-H bond develops that is centered deeper into the valence band. The same is true for the H-atom charge density (24%, 15%, and 7%, respectively). The charge density on the atom further away from the H atom increases (20%, 25%, and 31% for $\Delta=0$, 1.06, and 2.12 Å, respectively). Due to the dispersion, an increasing amount of this charge density is filled with electrons (0%, 1%, and 11%, respectively), and the unfilled charge is distributed over several states. Thus the character of the state in the vicinity of the gap is increasingly that of a dangling bond on the silicon atom further away from the H, as Δ increases.

E. Strain-energy relief in the neutral charge state

Finally, one calculation was also performed for H in its neutral state for $\Delta=0$ and asymmetrically placed at $\Delta=+1.06$ Å. Only minor relaxations occurred relative to the charged configuration (a 0.07-Å expansion of the perfect bond-center configuration, for example, giving an energy lowering of 0.04 eV) and the energy gains were approximately equal for the strained and nonstrained configurations. The resulting energy for transferring a neutral H to a strained bond was found to be 0.09 eV *more* favorable than in the positive state. Notice that this number is a third-order energy difference and is probably meaningful. Most of this energy difference (0.07 eV) comes from the half-filling of the midgap electronic state. Suppose we extrapolate this result to include also the symmetrically placed H atom. Then we should find that the energy gain for the H going off center would diminish as we fill the state in the gap. This is due to the state in the gap associated with the symmetric H position is placed lower than the state associated with the asymmetric H.

IV. DISCUSSION

The present calculations of hydrogen in strained Si-Si bonds apply to amorphous silicon and perhaps to hydrogen clusters in polycrystalline and crystalline silicon where there are distortions of the Si-Si bonds (in particular, the network disorder in *a*-Si:H is for small distortions taken up mostly by bond-angle distortions, analogous to our calculational setup). Grain boundaries in polycrystalline Si are another example of highly strained structures. Bond-angle strain is found in both tilt and twist boundaries,[12] and we would expect H atoms to accommodate this stress. This could also be true for the elements on the far left and right in the Periodic Table that bind weakly to Si,[10] and for vacancies. In agreement with our calculation on the stress-relieving effects of a vacancy is a finding that highly strained twist boundaries in Ge are sources and sinks of vacancies.[12] The platelet structures formed by hydrogenation of single-crystal Si have strained Si-Si bonds, but the extent of the bond-angle strain is unclear as the structure of the platelet edge is not determined.

Models of hydrogen in *a*-Si:H have assumed that hydrogen bonding is stronger at distorted Si-Si bonds. Furthermore, it has been suggested that the bonding site is highly asymmetrical at the most strained sites, approximating to a Si-H bond and a dangling bond rather than a bond-center site. The calculations confirm both of these suppositions. The asymmetrical site is favored by up to 1 eV and the electronic states in these sites have the character of a silicon dangling bond.

The variation of hydrogen binding energies in *a*-Si:H can be described by a hydrogen density-of-states distrbution. The calculations allow an estimate of this distribution, by relating the bond-angle disorder in *a*-Si:H to the strain-induced changes in the H bond. We assume a Gaussian distribution of bond-angle deviations, $N(\theta)$, with distribution σ, about the normal tetrahedral silicon bonding. The bond-angle deviation is about 10°, as obtained from x-ray measurements of the silicon radial distribution function,

$$N(\theta)=N_0\exp(-\theta^2/\sigma^2) \ . \tag{3}$$

The bond-angle deviation is related to the strain introduced in the calculations, approximately by Δ/R, where R is the bond length, 2.35 Å. The energy shift, E_H, of the hydrogen bond in Fig. 3 is roughly parabolic and may be described by

$$E_H=\alpha\Delta^2 \ , \tag{4}$$

with $\alpha\simeq0.4$ eV Å^{-2}. The distribution of the hydrogen-bond energy is therefore

$$N(E_H)=N_0\exp(-E_H/E_0) \ , \tag{5}$$

where

$$E_0=\sigma^2R^2\alpha\approx100 \text{ meV} \ . \tag{6}$$

Thus, we obtain an exponential hydrogen distribution with an inverse slope of 100 meV.

This distribution is close to the estimates made previously for the hydrogen density of states in *a*-Si:H, which were based on simple models of weak bond breaking.[13] Again the calculations support the previous model.

V. SUMMARY

We have found that H can relieve strain energy, and that the "weak-bond" model[5,6] is confirmed in three ways: (i) the H atom preferentially bonds with one of the Si atoms, and the preference becomes stronger as the angular stress increases; (ii) the electronic midgap state becomes more and more similar to a dangling bond as the angular stress increases; and (iii) the total energies at these strained sites in combination with the known bond-angle distribution gives a H bond energy distribution in agreement with experimental findings.

Interestingly enough, we find that H is a good stress reliever, but not the best. A vacancy would be about 2 times better. This implies that superior stress relief might be obtained for elements that bond very weakly to the substitutional site in Si. These would be the elements on the far right and far left of the Periodic Table.[10] It is noteworthy that for these elements the electronic states become more and more vacancylike, which means that with a high probability these strained substitutional sites could have a negative effective electronic correlation energy.[10,14] The intriguing possibility then arises that with these impurities one could have the stress-relieving effects of H, the negative-U behavior of the vacancy, and lose the unfavorable effects of the fast-diffusing H atoms on structural metastability.

ACKNOWLEDGMENTS

Discussions with Dr. Warren Jackson and a critical reading by Matthias Schabel are acknowledged. The research was supported by the U.S. Office of Naval Research through Contract No. N00014-82-C-0244 and by the Solar Energy Research Institute.

---

[1] See, for example, R. A. Street, in *Hydrogen in Semiconductors: Bulk and Surface Properties*, edited by M. Stutzmann and J. Chevallier (North-Holland, Amsterdam, 1991), p. 69.

[2] R. A. Street, Solar Cells **24**, 211 (1988).

[3] C. G. Van de Walle, in *Hydrogen in Semiconductors*, edited by J. I. Pankove and N. M. Johnson, Vol. 34 of *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, Boston, 1991), p. 585.

[4] See, for example, W. Schulke, Philos. Mag. B **43**, 451 (1981).

[5] Z. Smith and S. Wagner, Phys. Rev. Lett. **59**, 688 (1987).

[6] R. A. Street and K. Winer, Phys. Rev. B **40**, 6236 (1989).

[7] R. Biswas, I. Kwon, and C. M. Soukoulis, in *Amorphous Silicon Technology—1991*, edited by Arun Madan, Y. Hamakawa, M. J. Thompson, P. C. Taylor, and P. G. LeComber, MRS Symposia Proceedings No. 219 (Materials Research Society, Pittsburgh, 1991), p. 99.

[8] See, for example, J. D. Joannopoulos, in *Physics of Disordered Materials*, edited by D. Adler, H. Fritsche, and S. R. Ovshinsky (Plenum, New York, 1985), and references therein.

[9] For the configuration with the asymmetrically placed H, the first-order changes between 7 and 9 Ry were 0.12 eV; between 9 and 11 Ry, 0.01 eV; and between 11 and 13 Ry, −0.05 eV. For the configuration without H, however, the first-order changes between 7 and 9 Ry, were 0.13 eV, and between 9 and 11 Ry, also 0.13 eV. The discrepancy can be explained as follows. The electronic states in the small unit cell of the distorted structure without H mix with the conduction-band states. Since the size of the band gap decreases with increasing cutoff energy, the convergence becomes artificially slow. This effect is absent in the large 32-atom unit-cell calculation, except for the largest distortion; only for the latter is there any mixing of the valence- and conduction-band states.

[10] E. Tarnow, Europhys. Lett. **17**, 157 (1992).

[11] A proposal for the true nature of the antibonding state was given by R. Fisch and D. C. Licciardello, Phys. Rev. Lett. **41**, 889 (1978). This proposition was confirmed by S. F. J. Cox and M. C. R. Symons, Chem. Phys. Lett. **126**, 516 (1986).

[12] See, for example, E. Tarnow, T. Arias, P. D. Bristowe, P. Dallot, G. P. Francis, J. D. Joannopoulos, and M. C. Payne, in *Atomic Scale Calculations of Structure in Materials*, edited by M. S. Daw and M. A. Schlüter, MRS Symposia Proceedings No. 193 (Materials Research Society, Pittsburgh, 1990).

[13] R. A. Street, Solar Cells **30**, 207 (1991).

[14] For a review of the properties of the vacancy, see G. D. Watkins, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 147.