Dangling Bond in *a*-Si:H

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(Received 5 February 1986)

The configuration-coordinate diagram for a model dangling-bond geometry is obtained by *ab initio* total-energy calculations. The results yield equilibrium geometries for different charge states, thermodynamic and optical transition energies, large Stokes shifts (0.5–0.6 eV), and a *negative* effective correlation energy (-0.2 ± 0.2 eV). Implications of these results for the current experimental and theoretical understanding are discussed.

PACS numbers: 71.25.Mg, 61.40.+b, 81.40.Rs

The dominant defect in tetrahedrally bonded amorphous semiconductors is believed to be intrinsic, and associated with a threefold coordinated atom or dangling bond. It is thought to be responsible for electronic states within the material's semiconductor gap, and is believed to play an essential role in determining many structural, electronic, and transport properties of both pure and hydrogenated samples.[1]

While macroscopic properties are often attributed to the dangling bond very little is actually known about the microscopic structure of tetrahedral amorphous semiconductors (the most studied being silicon) and its defects. In particular, the common experimental spin signal from tetrahedrally bonded amorphous semiconductors is attributed to positive-correlation-energy dangling bonds. Conventionally it is believed that in unhydrogenated samples, Fermi-energy pinning is due to the large density of dangling-bond states in the semiconductor gap, as indicated by the spin signal. In contrast, hydrogenated samples have fewer dangling bonds which, therefore, allows doping.[2]

More recently, evidence has been presented that dangling bonds are created in the doping of *a*-Si:H,[3] and thus, that they play an even more essential role in the doping mechanism. An intriguing counterpoint to the role of dangling bonds in the doping process are light-induced metastable dangling bonds believed to be responsible for the dramatic changes in material properties under illumination known as the Staebler-Wronski effect.[4]

Many experimental studies have been dedicated to inferring properties of the dangling bond in *a*-Si:H.[1] While the spin signal suggests a positive correlation energy, interestingly, Adler[5] has described evidence for a negative effective electron-electron repulsion. However, other experiments[6–9] have supported a positive effective repulsion energy.

We approach the problem of understanding the dangling bond in an amorphous material in two steps. First, we choose a particular model for the dangling bond and, with *ab initio* total-energy calculations,[10] obtain its properties—structure (minimum energy positions of the atoms for different charge states), optical transitions, Stokes shifts, thermodynamic transition energies, bare correlation energy, and effective correlation energy. From these calculations emerges the possibility of negative-effective-correlation dangling bonds, which compels a reevaluation of the current understanding of the amorphous material. Second, we further develop our understanding of the dangling bond by studying how the amorphous nature of the material affects its properties. Here we use a model to understand the effect of simple structural variations of the host surrounding the dangling bond. Certain defect properties, particularly transition energies, are found to be quite sensitive to the environment. However, the effective correlation energy does not vary enough to account for the large positive values suggested by most experiments. This leads us to propose a new picture for the nature of dangling bonds in *a*-Si and *a*-Si:H.

The dangling-bond model geometry, which we use in our total-energy calculations, has been studied by Bernholc[11] using Green's function techniques. He found the bare electronic repulsion energy (without structural relaxation) to be 0.5 eV. Our result for the bare electronic repulsion energy is in close agreement with Bernholc's; however, the total-energy surfaces we calculate show that strong electron-driven relaxations lead to a negative effective electron-electron repulsion with a calculated value -0.2 ± 0.2 eV.

In Fig. 1 we schematically display the simplest structural model[11] for the dangling bond in *a*-Si:H—a triply hydrogenated vacancy in a crystalline environment. In our calculations we evaluate the total energy of this defect for many positions of the atoms. We focus on two structural parameters (Fig. 1): u is the motion of the atom which has the dangling bond towards and away from the triangle formed by its three nearest neighbors, and v is the motion of the three nearest neighbors away from the (original) position of the threefold coordinated atom. Total energies were obtained using momentum-space pseudopotential density-functional theory in the super-cell approximation.[10] Most results were obtained in super cells containing sixteen bulk atoms. Convergence in super-cell size was tested using super cells containing from 8 up to 64 bulk atoms. The hydrogen atoms and silicon

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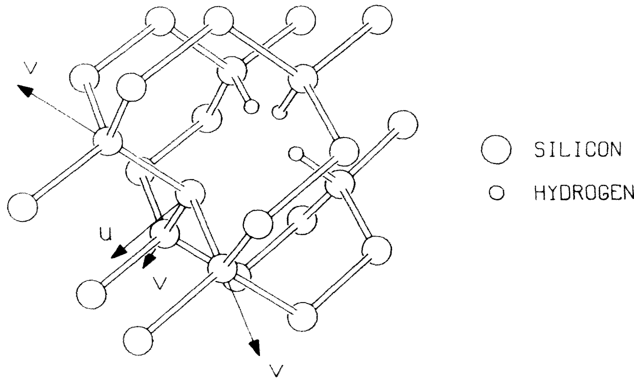

FIG. 1. Dangling-bond model geometry with structural parameters (u, v) indicated.

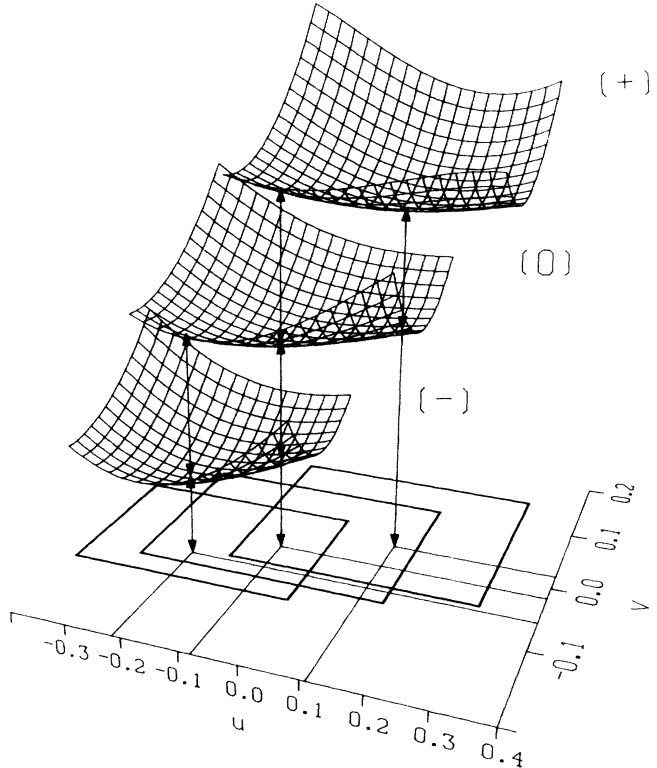

FIG. 2. Total-energy surfaces of the dangling-bond model geometry for charge states $(+, 0, -)$ plotted as a function of the (u, v) coordinate space indicated in Fig. 1 (units are bulk bond lengths).

atoms bonded to them were initially allowed to relax, and then frozen for the remainder of the calculations. The Si—H bond length was found to be close to the standard experimental value, and the silicon atoms were found to relax away from the vacancy by 5% of the bulk Si—Si bond length. The reference point for transition-state energies is obtained as follows. Calculations are first fixed with respect to the silicon-bulk valence edge. This edge is then assumed to lie above the a-Si:H mobility edge by 0.5 eV as is commonly believed to be the case. This procedure leaves some uncertainty in the transition-level energies (~ 0.3 eV); however, it does not affect the correlation energies we obtain, or conclusions presented herein.

Total energies were obtained for three charge states $(+, 0, -)$ for many different values of (u, v). The two-dimensional (u, v) energy surfaces, separated vertically for greater visibility, are shown in Fig. 2. The minimum-energy configurations of each charge state were found, and are projected onto the (u, v) plane. The domain of plotted energy values of each charge state is indicated by rectangles on the (u, v) plane. In Fig. 3 an effective one-dimensional configuration-coordinate diagram has been constructed in the natural way by plotting energy values for two vectors: from the minimum-energy configuration of the neutral charge state—looking towards that of the negative charge state; and from the minimum-energy configuration of the neutral charge state—looking towards that of the positive charge state. We show all four excitation transitions as up arrows and all four luminescence transitions as down arrows. For convenience we include two curves for the neutral charge state; one, with an excited electron-hole pair, is higher in energy by the semiconductor gap. As an aid to interpretation, to the right are schematic diagrams showing the occupation of the dangling-bond orbital and the presence of an electron or hole in the conduction or valence band. Other properties of the dangling bond can be obtained from Fig. 3. For example, it is easy to see the large electron-driven relaxations which yield Stokes shifts of 0.5–0.6 eV.

In Table I we collect and compare our theoretical

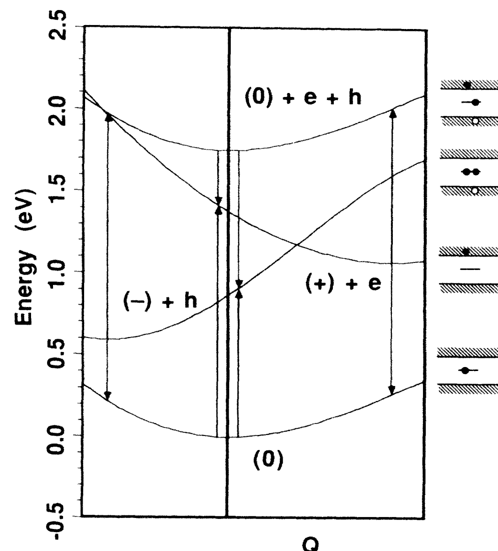

FIG. 3. Configuration-coordinate diagram constructed for the dangling bond from the total-energy surfaces of Fig. 3 (see text).

TABLE I. Comparisons between theoretical calculations on the model dangling-bond geometry as described in the text and selected values inferred from a variety of experiments on a-Si:H.

	Theory	Experiment
ϵ optical		
$(+\rightarrow 0)$	0.94	Broad Peak
$(0\rightarrow -)$	0.87	0.8–1.4
$(-\rightarrow 0)$	1.38	Shoulder at 0.5[a]
$(0\rightarrow +)$	1.38	
ϵ luminescence		
$(+\rightarrow 0)$	0.37	
$(0\rightarrow -)$	0.37	Peak at ~0.9[b]
$(-\rightarrow 0)$	0.88	
$(0\rightarrow +)$	0.81	
Stokes shift	0.5–0.6	0.1[a]; 0.4–0.5[b]
Hubbard U	0.45 (0.5[c])	~0.6–0.8[a]
Effective U	-0.2 ± 0.2	0.5[a,b]

[a]Reference 9.
[b]Reference 12.
[c]Reference 11.

results on this model dangling bond to values which have been inferred from a variety of experiments. Experimental values are representative, not exhaustive. Overall, the comparison can be seen to work in some cases, but not in others. The comparison between theory and experiment seems to break down in the most severe way for the effective correlation energy. While other values have appeared in the literature, as previously mentioned, experimental values have congregated around +0.5 eV, while our value for this model dangling-bond geometry is -0.2 ± 0.2 eV.[13] The theoretical value reflects the strong electron-driven relaxations and includes a small (−0.05 eV) contribution from relaxation of more distant atoms through a Keating-model[14] approximation. Error bars arise from internal convergence errors (including super-cell size) of 0.1 eV and an estimate of systematic error of 0.1 eV (reasonable because of error cancellation in the second-order difference for correlation energies).

The next step in our study of the dangling bond is to model the effects of the amorphous nature of the material in which it is located. Motivated by the results just described, we focus on thermodynamic transition energies and the effective correlation energy. It is important to see whether the experimentally inferred large positive (0.5 eV) correlation energy can arise from simple variations in host geometry.

In an amorphous material, variations in the positions of atoms in the neighborhood of the dangling bond should have the primary effect of changing the equilibrium size of the triangle formed by the nearest neighbors of the threefold coordinated atom (see Fig. 1). To model this effect we simply apply a force along v which changes the equilibrium size of the triangle

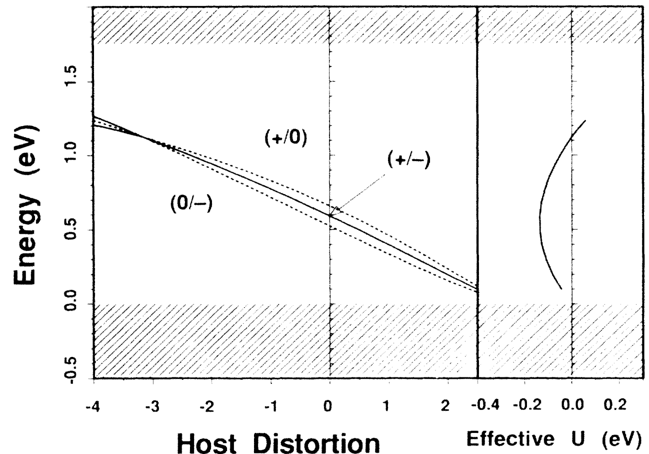

FIG. 4. Dangling-bond thermodynamic transitions and effective correlation energy as a function of host distortion (see text).

but we still enable both the threefold coordinated atom and its nearest neighbors to relax. With this simple model we can plot dangling-bond properties as we vary the host structural distortion. We limit the range of variation by requiring that equilibrium bond lengths are not distorted by more than 5% of the bulk length (beyond which the structure is likely to be unstable). Through this model we can estimate the range of defect properties which may be expected in an amorphous material.

In the main panel of Fig. 4 we show the variation of thermodynamic transition energies of the dangling bond as a function of host distortion. Valence and conduction bands are shown as shaded areas. Because of the negative effective correlation energy (U), a two-electron thermodynamic transition $(+/-)$ superceeds the transitions $(+/0)$ and $(0/-)$. The latter transitions are nevertheless shown at their virtual energies, with $(+/0)$ higher than $(0/-)$. The undistorted host is indicated by the auxiliary vertical axis. While the undistorted-host transition energy is 0.6 eV we see that this value is very sensitive to structural variation leading to a large range of transition energies within the gap. In the right panel we show the dependence of the effective correlation energy (which can be directly obtained as the difference between the two virtual one-electron transition energies) on transition energy. Host distortion in either direction raises the effective correlation energy towards positive values. However, the largest positive value obtained is 0.05 eV. Thus, at least for this model, we do not find values as large as the 0.5 eV obtained from some experiments,[6–9] or large negative values from other experiments.[5] The correlation between the effective correlation energy and the thermodynamic transition energy, as well as the dependence of other properties such as optical transitions on the position of the ther-

modynamic transition energy, may have important implications for interpretation of experiments.

The results presented here lead us to propose a new picture for the dangling bond in tetrahedrally bonded amorphous materials. Theoretical calculations we described—for a model dangling-bond geometry including simple host structural variations—indicate that the experimentally observed correlation energy is not characteristic of dangling bonds in general. Instead, we must surmise that it reflects the properties of a particular type of dangling-bond geometry (or class of geometries). We conclude that it will be necessary to identify the type of dangling bond which is dominant in the material under different circumstances and not assume that they are all the same (for example the dangling-bond type may vary with hydrogenation, irradiation, or doping). Secondly, if a particular dangling-bond type predominates then we should identify the mechanism which produces it. An example is hydrogenation; *a*-Si:H has 10^{-3} times the number of dangling bonds as *a*-Si, which may imply a selection process enhancing the survival of a certain dangling-bond geometry and its associated properties. On the other hand, several types of dangling bond may survive hydrogenation.

These results have important implications for structural models of *a*-Si and *a*-Si:H since the number of dangling bonds as currently counted by electron-spin resonance may not include substantial numbers of negative correlation defects, thus underestimating this important measure of network structural frustration.[15]

This work was supported in part by National Science Foundation Grant No. DMR 84-18715. We thank D. Adler for helpful discussions. One of us (Y.B.) is a Bantrell Post-Doctoral Fellow.

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[13]A simple estimate of the correlation energy based on generalized-valence-band cluster calculations in an effective medium was given in Ref. 1, p. 50, as 2.5 eV for an isolated dangling bond on a surface and ≤ 1.0 eV for a bulk dangling bond. These results involved an effective-medium correction to the Hubbard energy which, in light of current results, turns out to be too small. [A rough estimate of the difference between the Hubbard U and effective U can be extrapolated from vacancy calculations of G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B **21**, 5662 (1981). The result (~ 0.1 eV) is much too small because the large dangling-bond relaxations are beyond the harmonic regime assumed in that work.]

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