

## First-principles simulations of *a*-Si and *a*-Si:H surfaces

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We use *ab initio* local-density-approximation methods to develop an *ab initio* model of an *a*-Si and an *a*-Si:H surface. Starting with a supercell of bulk *a*-Si, we remove periodic boundary conditions in one direction and relax the sample using *ab initio* methods. H is added to remove bulk defects. The surface structure and coordination of atoms is discussed, and defect states are characterized. H is added to dangling bonds on the *a*-Si:H surface, creating a hydrogen-terminated *a*-Si:H surface. We explore the relationship between electronic and geometric surface defects.

### I. INTRODUCTION

With the increasing use of hydrogenated amorphous silicon (*a*-Si:H) in many large-area electronic devices, it becomes ever more important to understand the material at an atomistic level. Solar cells, thin-film transistors and several kinds of imaging devices all use thin films of *a*-Si:H. All commercial films are deposited using plasma assisted chemical vapor deposition, a process whose reaction pathways are not fully understood. An obvious prelude to modeling growth is to understand the structure of the amorphous surface. The main point of this paper is to present an *ab initio* study of an *a*-Si and an *a*-Si:H surface.<sup>1</sup> We elucidate defect structure and surface geometry and study the relationship between electronic and geometric defects.

During PACVD, silane gas (SiH<sub>4</sub>) is pumped through a set of parallel plate electrodes, where rf or dc power drives one electrode and creates a plasma discharge. This discharge breaks up roughly 10% of the silane molecules into neutral radicals, primarily SiH<sub>3</sub>, which constitute the reactive flux. This flux impinges upon a substrate which is heated to 150–300 °C. Usually, H<sub>2</sub> is added to produce better quality films. Experiments have ascertained that typical high-quality films have a bulk H concentration of 15–25 at.%, a band gap of 1.7–1.8 eV, and a density of electronic states in the band gap of  $2 \times 10^{15}$  cm<sup>-3</sup>. Abelson<sup>2</sup> summarized the current state of knowledge of the growth surface of *a*-Si:H by PACVD. Recently, Stutzin *et al.* used STM to study the topography of the as-grown surface of *a*-Si:H.<sup>3</sup> They imaged 100-, 1000-, and 4000-Å-thick films of intrinsic device-quality material. The 100-Å-thick films were found to be flat within two atomic layers and had typical rms height variations of  $\sim 2$  Å, while the thicker films had a much more

varied topography. In these films, Stutzin *et al.* found regions where undulations of  $\sim 40$  Å height were next to atomically flat areas. While the scale of the STM study is too large to allow a quantitative comparison of the topographies of an actual surface and our model surface, we find it encouraging that flat regions are observed that are qualitatively similar to the model.

We now give a brief review of the computational work done to model *a*-Si:H. These efforts fall into one of two broad categories: semiempirical methods and first-principles methods. Recently, Holender *et al.*<sup>4</sup> used their large cell of *a*-Si and created a model of bulk *a*-Si:H by removing under- and overcoordinated atoms and passivating the dangling bonds with H. They used a phenomenological many body potential to do classical molecular dynamics on the system and calculated the electronic properties via a method combining the equation of motion technique and Chadi's tight binding model.<sup>5</sup> The resulting structure has only fourfold-coordinated Si, 23 at.% H, a density 0.827 that of *c*-Si, and partial radial distribution functions (PRDF's) in good agreement with experiment.

Wooten, Weaire, and Winer<sup>6</sup> developed a 216-atom model of bulk *a*-Si from a *c*-Si initial configuration. The process involved bond switching, partial relaxation of the structure using the Keating potential,<sup>7</sup> and a Maxwell-Boltzmann factor to allow the structure to escape from a metastable state to an amorphous state with lower energy. They calculated the radial distribution function (RDF) for their structure, scaled it, and compared it to the experimental RDF for *a*-Ge. The RDF was in satisfactory agreement with experiment. While the model was structurally reasonable, it had difficulties with its electronic structure, particularly with regard to the bandtailing.<sup>8</sup>

For the surface, Gleason *et al.*<sup>9</sup> did Monte Carlo simulations to obtain *a*-Si:H slabs with 400–1000 atoms. They

required all Si-Si bond lengths to be within 1% of the nearest-neighbor bond in *c*-Si, and allowed bond angles to vary no more than 5° from the tetrahedral angle. All Si atoms were required to have four bonds, i.e., no dangling or floating bond defects were present. A model surface was “grown” in two stages: first, a SiH<sub>4</sub> precursor was allowed to bond in one of four different ways to the existing surface; second, any other possible Si-Si bonds were formed between the precursor and the surface, with the resulting elimination of H. The authors also introduced etching and surface diffusion into the model. The final structures had H concentrations in the range 11–44 at.%. Gleason *et al.* were primarily interested in the geometric structure of the surface; their method did not investigate the electronic structure of the *a*-Si:H film produced. We are concerned that the geometrical constraints that Gleason *et al.* placed upon the structure are too stringent. For example, experimentally it is observed that the bond angles in *a*-Si:H have a rms deviation of 10°. More importantly, we are concerned about the quality of the empirical potential that Gleason *et al.* used to model Si-H interactions.

There are also *ab initio* studies of bulk *a*-Si and *a*-Si:H. Drabold *et al.*<sup>11</sup> created a 63-atom cell of *a*-Si. They made a vacancy in a 64-atom sample of *c*-Si, heated it, and then did a simulated anneal with *ab initio* methods. They also relaxed several models that were originally obtained using semiempirical methods, including the 216-atom WWW cell. Models of bulk *a*-Si:H were developed by Fedders and Drabold<sup>8</sup> and by Buda *et al.*<sup>12</sup> Fedders and Drabold used the Sankey-Drabold local orbital code to create and examine *a*-Si:H supercells with 66–71 atoms. These models had 0–2 well-localized defects. They also probed the role of H in passivating dangling bonds and simulated H sitting in a variety of positions in the cells. These cells all have good agreement with experimental pair correlation functions, bond angle distributions, vibrational spectra, and defect densities. Buda *et al.* developed a 72-atom model of bulk *a*-Si:H. They obtained it by first placing eight H atoms at the interstices of a *c*-Si sample, heating this structure until it became a liquid, equilibrating the liquid, and then doing a rapid quench. All this was carried out using the molecular-dynamics method developed by Car and Parrinello.<sup>13</sup> Their calculated partial pair-correlation functions were in good agreement with experiment. They found overcoordinated Si and weak, i.e., long bonds between several Si-Si and Si-H pairs. The Si-H weak bonds disappeared upon annealing. They also found H residing in a microcavity due to two missing Si.

We have examined some of the simulations performed on amorphous silicon. Following the reasoning of Fedders *et al.*,<sup>14</sup> we note that while semiempirical methods have the advantage of being able to handle large numbers of atoms, thereby reducing finite-size effects, such potentials are not transferable between different bonding environments. Since the detailed atomic structure of a typical *a*-Si:H surface is unknown at the present, we use an *ab initio* method that has the flexibility to handle the variety of bonding geometries that might be observed. The next section contains a brief overview of this method

and a description of the procedure by which we obtained a model for a clean *a*-Si surface.

## II. METHOD

All calculations were done using the Sankey-Drabold density functional local-density-approximation (LDA) code.<sup>15</sup> In addition to the LDA, further approximations are incorporated in this method. First, it uses a non-self-consistent version of density functional theory by using a linearized form of the Kohn-Sham equations due to Harris<sup>16</sup> and Foulkes and Haydock.<sup>17</sup> Second, we approximate the one-electron energy eigenstate as a linear combination of pseudoatomic orbitals (PAO's),<sup>18</sup> computed from a self-consistent Herman-Skillman-like program.<sup>19</sup> We impose a confinement boundary  $R_c$  on the PAO's to reduce the number of neighbors interacting with a site; beyond  $R_c$  there is no interaction. We use an  $R_c$  of  $5.00a_0$  for Si and H: this corresponds to third-neighbor interactions for Si. Applications of this method to Si clusters<sup>20</sup> and crystal surfaces<sup>21</sup> yielded structures, bond lengths, and vibrational frequencies in very close agreement to fully self-consistent LDA calculations.

We begin with the WWW 216-atom cell of bulk *a*-Si, as relaxed by Fedders, Drabold, and Klemm. This cell has one geometrical defect complex, consisting of two fivefold-coordinated atoms and a sixfold-coordinated atom. The supercell is a cube 16.1 Å on edge. To go from a supercell with periodic boundary conditions in three dimensions to an infinite slab, we first remove the periodicity in one dimension. We arbitrarily designate one surface as the “bottom” and one as the “top.” On the bottom surface are many dangling bonds, created by the loss of the atoms from the image cell which existed below this cell in the bulk calculations. We passivate these bonds with hydrogen atoms, placed along the former bond line at a distance of 1.5 Å from the Si to be passivated.

As much as possible, we want to mimic a half-space of *a*-Si:H, with only one free surface. To this end we fix the bottom Si in their bulk positions. To maintain the orientation of the bonds of these Si, the passivating H are also fixed in their starting positions. The sample of 216 Si and 34 H was then relaxed by simulated quenching using the S-D code with the  $\Gamma$  point and a time step of 2.00 fs. This approximation for the Brillouin zone integrals was tested by Fedders *et al.*<sup>14</sup> A force tolerance of  $1 \times 10^{-1}$  eV/Å was used to determine when the structure was relaxed.

After relaxing the sample for 0.6 ps, we observed that the forces on the unfixed atoms were below or very close to the tolerance. The average force on the fixed atoms, though, was unacceptably large, indicating that these atoms did not want to remain in their *a*-Si bulk positions. The charge localization for this structure, computed as described below, showed that of the five most localized states in the band gap, four of these were centered primarily upon fixed atoms. In an attempt to improve this obvious finite-size effect, we freed all fixed atoms. With

all atoms free to move, the structure relaxed in 0.6 ps to the configuration discussed in Sec. III. The average force per atom was  $0.021 \text{ eV/\AA}$ , with a maximum force of  $0.13 \text{ eV/\AA}$ . As in all simulations, we look to avoid or at least identify effects caused by the limited size of the model we use. Although there is no direct interaction between the top and bottom surfaces, the *a*-Si network transmits forces from one surface to the other. During the relaxation with all atoms free, we find that the bottom surface atoms undergo a comparatively large average displacement of  $0.49 \text{ \AA}$ , as expected. The major finite-size effect is that the top surface atoms move also, with an average displacement of  $0.21 \text{ \AA}$ .<sup>22</sup> We discuss the resulting *a*-Si surface in more detail in the next section.

### III. *a*-Si SURFACE

Our model for a clean *a*-Si surface is shown in Fig. 1. For clarity, we show only those atoms that are no more than  $5.3 \text{ \AA}$  below the top atom. We have employed periodic boundary conditions in the *x* and *y* directions to show all the bonds from these surface atoms to atoms in neighboring cells. This results in a picture that displays all the contour of the surface. We distinguish threefold-coordinated atoms from the others as these atoms are the sites of most of the localized states. The number density function  $n(r)$  has its first minimum at  $r = 2.78 \text{ \AA}$ , and we define this distance to be the maximum Si-Si bond distance. We then determine the coordination of all atoms in the model. We observe three classes of coordination: Table I lists the number of atoms of each coordination. There are eleven threefold-coordinated atoms and seven fivefold-coordinated atoms on the surface: this is 92% of

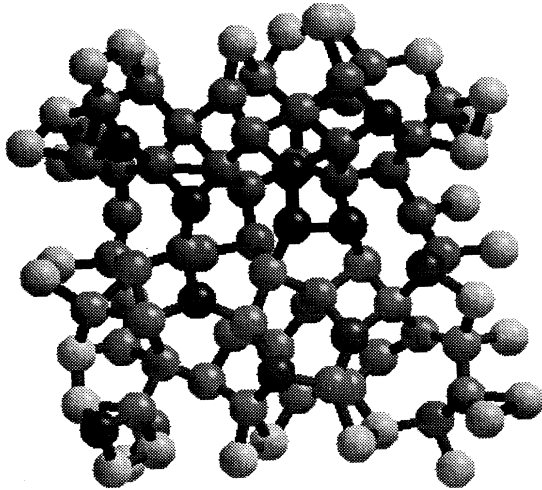


FIG. 1. Picture of a clean *a*-Si surface. The view is from above along the *z* axis. The periodic boundary conditions in the *x* and *y* directions have been used to show bonds between surface atoms and atoms in the image cells. The different shades of the atoms signify the following: light, atoms in neighboring cells; medium, fourfold- and fivefold-coordinated Si atoms; dark, threefold-coordinated atoms.

TABLE I. Coordination of Si atoms in an *a*-Si surface model.

No. of neighbors	No. of atoms
3	12
4	194
5	10

all threefold-coordinated atoms and 70% of all fivefold-coordinated atoms in the sample.

Because the coordination of an atom depends upon the choice of “bond length,” and because the fundamental and relevant definition of a defect depends on the electronic structure, we study the localization of electronic states in the supercell. We calculate a “localized charge”  $q(n, E)$  for each eigenvalue with energy  $E$  and the atomic site centered on atom number  $n$ . A mean-square charge<sup>14</sup> was calculated for each eigenvalue  $E$  by

$$q_2(E) = \sum_n q(n, E)^2. \quad (1)$$

Defining  $Q_2(E) = Nq_2(E)$  with  $N$  the number of atoms in the sample, we have a measure of the localization of a given band. Figure 2(a) plots  $Q_2(E)$  versus  $E$  for the

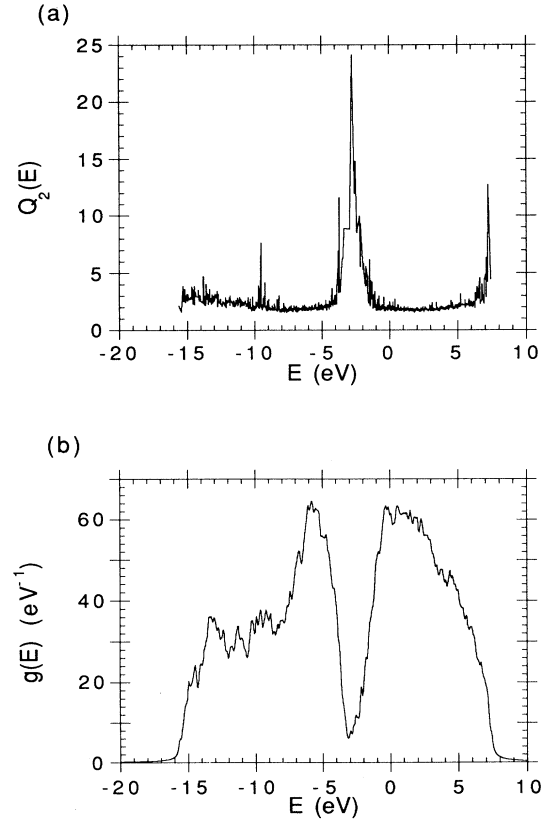


FIG. 2. (a) Charge localization for the clean *a*-Si surface.  $Q_2(E)$ , defined in the text, is plotted vs the energy of the eigenvalues. (b) Electronic DOS for the clean *a*-Si surface model. The  $\delta$  function in the expression for  $g(E)$  is Lorentzian broadened (width =  $0.5 \text{ eV}$ ).

clean surface. We define an electronic defect to be any eigenvalue with  $Q_2(E) > 4$ . For each of these eigenvalues, we determine the atoms where the charge is most strongly localized. We are particularly interested in those localized eigenvalues whose energies are in the band gap. A much-debated question in the study of *a*-Si concerns the extent of the relationship between these electronic defects and the bonding geometry of the atoms on which they are localized. For the localized eigenvalues, we determine the atoms where the charge is most strongly localized and look at the arrangement of the bonds. We find electronic defects residing on three different types of bond arrangements, examples of which we explain below.

Figures 3(a)–3(c) show sketches of the surface defects. These sketches show only bond angles which vary more than  $10^\circ$  from  $109.5^\circ$  and bond lengths which are substantially longer than the *c*-Si nearest-neighbor distance of 2.35 Å. The drawings are not to scale, and the numbers assigned to various atoms are for reference purposes only. Figure 3(a) shows the threefold-coordinated atom, which is the simplest surface defect. The eigenvalue most strongly localized at the surface is centered on atom 36. Of the 19 localized eigenvalues, eight are located on threefold-coordinated surface atoms. Seven spectral defects were localized on fourfold-coordinated surface atoms. These atoms turned out to be in highly distorted bonding environments. Figure 3(b) shows an example of this. We call this the *S*. Several bond angles deviate substantially from the tetrahedral bond angle. This atom is clearly not favorably bonded to its neighbors. One spectral defect was centered upon a fivefold-

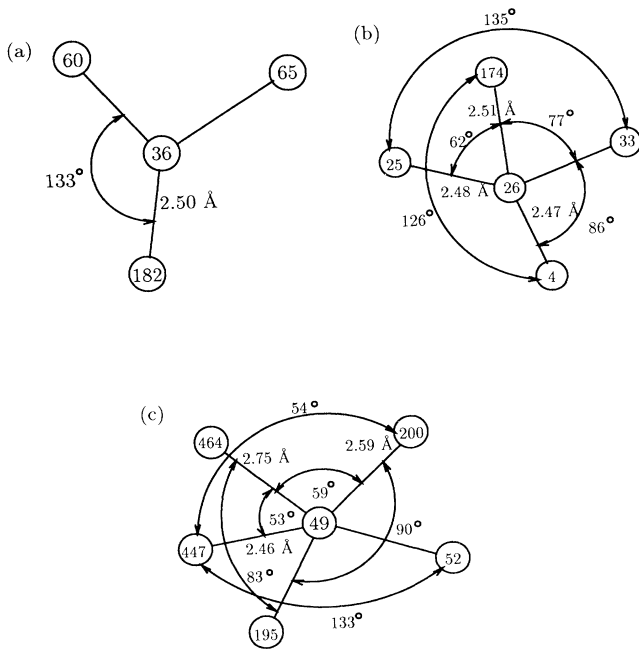


FIG. 3. Sketches of the bonding arrangement for (a) the threefold-coordinated surface defect, (b) the *S* defect, and (c) the fivefold-coordinated defect. In the *S* defect, the heights of the other atoms, relative to atom 26, are as follows: atom 4,  $-1.5$  Å; atom 25,  $-0.6$  Å; atom 33,  $-0.6$  Å; and atom 172,  $-0.7$  Å.

coordinated atom. Figure 3(c) displays the bonding arrangement; note the long bonds between atom 49 and atoms 200, 447, and 464. The bond angles vary greatly from  $109.5^\circ$ .

Figures 4(a)–4(c) give a measure of the spatial localization of the eigenvalues corresponding to the defects shown in Fig. 3. The sample is divided into 35 slices in the *z* direction. For each slice,  $Q_2(E)$  from each atom in the slice is added together. The total  $Q_2(z)$  for each slice

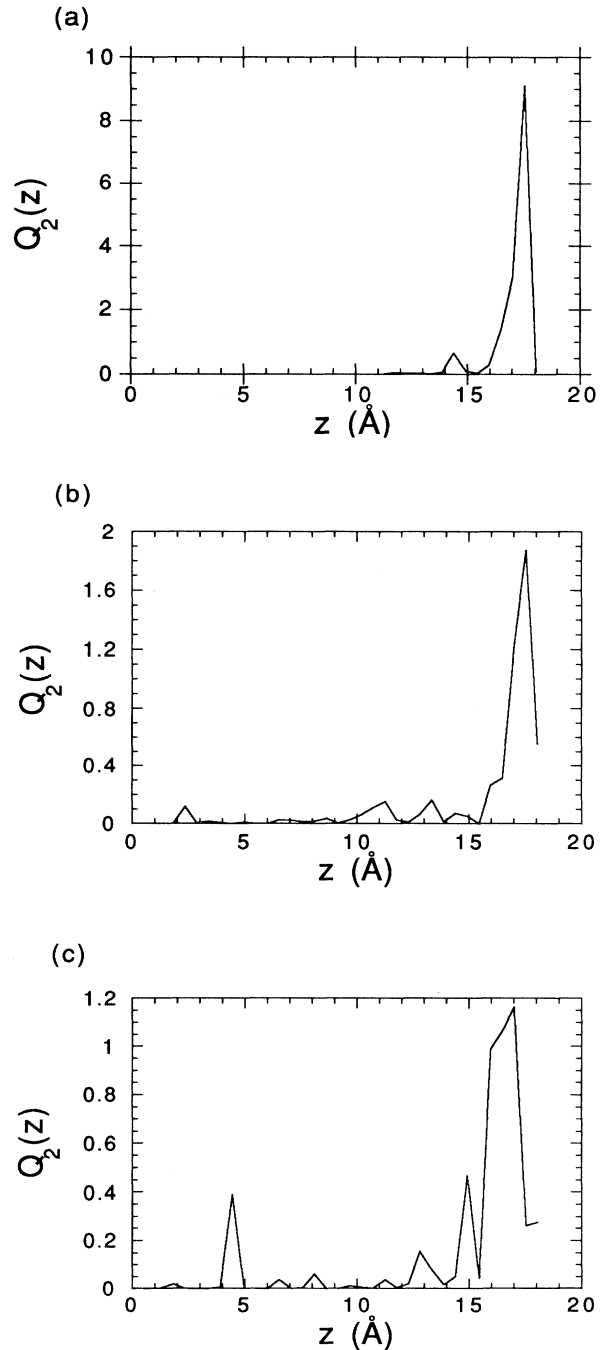


FIG. 4. Spatial charge localization for the eigenvalues associated with (a) the threefold defect, (b) the *S* defect, and (c) the fivefold defect.

is plotted versus the  $z$  coordinate of the center of the slice. We see from Fig. 4(a) that the eigenvalue for the threefold defect is quite localized in the surface region which contains atom 36. Figure 4(b) shows the spatial charge localization for this eigenvalue associated with the defect. The degree of localization is markedly less than that for the threefold defect. Figure 4(c) shows the charge localization for the fivefold defect. This is the least localized of the three defects discussed in this section. The deep penetration of this defect state into the bulk is presumably due to resonances with bulk defects at energies similar to the surface defect state.

We calculated the electronic density of states for this surface; it is shown in Fig. 2(b). The Fermi level is  $E_F = -3.0$  eV. The surface valence and conduction band edges were determined by looking at the charge localization for states near the Fermi level.<sup>14</sup> The valence band maximum  $E_v$  was taken to be the highest energy occupied, extended eigenvalue. In a similar way, the conduction band minimum  $E_c$  was chosen to be the lowest energy extended eigenvalue above the Fermi level. We found that  $E_v = -3.9$  eV and  $E_c = -1.9$  eV, which results in a band gap of  $E_g = 2.0$  eV. Our estimation of the band gap is larger than the measured values of 1.3–1.4.

#### IV. *a*-Si:H SURFACE

Experimentally, it is known that H assists the growth of *a*-Si:H by diffusing into the network and passivating defects such as Si dangling bonds. Due to the difference in time scales between such a diffusion process and this simulation, we cannot model the actual diffusion of H into the network. Instead, we place H at places which are probable destinations for diffusing H. Several electronic defects near the Fermi energy were localized on atoms in the bulk region of the *a*-Si structure. Because defects in the bulk affect surface states and structures, we attempted to remove as many of these bulk defects as possible. The technique for treating these defects has been developed earlier;<sup>8</sup> we do not describe them in detail here. Addition of H to the bulk region effectively created *a*-Si:H, albeit with a rather low H concentration: the “bulk” H concentration is 2 at.%. In computing this number, we ignore those H that are bonded to either surface. While this concentration is much lower than the usual 15–25%, *a*-Si:H films have been deposited with a bulk H content of 2–4%.<sup>23</sup> In fact, at higher H concentrations it is suspected that much of the H coats voids with relatively little distributed through the network.

Figure 5 shows the hydrogen-terminated surface of *a*-Si:H. As mentioned earlier, H has been added farther down in the *a*-Si sample to passivate defects and create *a*-Si:H. Table II gives the coordination of the structure. Threefold-coordinated atoms are eliminated from the structure, because H was added to dangling bond sites and removed the localized eigenvalue. H was added above the fourfold-coordinated atoms associated with spectral defects. This situation shows the importance

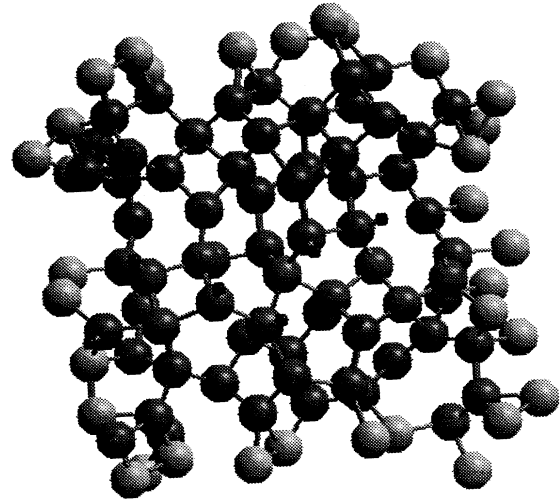


FIG. 5. Hydrogen-terminated *a*-Si:H surface. The shading of the Si atoms is the same as for the *a*-Si surface. There are no threefold-coordinated atoms on the surface. H atoms are in black.

of regarding the surface from an electronic structure perspective: the new fivefold-coordinated surface defect has a much less localized eigenvalue than it did as a fourfold-coordinated atom in the clean *a*-Si surface.

We calculate the charge localization for the eigenvalues of this structure and display it in Fig. 6(a). There are eleven localized eigenvalues near the Fermi energy of  $E_F = -2.7$  eV. Of these, seven are centered upon fourfold-coordinated atoms and three upon a fivefold-coordinated surface atom. The remaining one is upon an atom in the bulk. For comparison, in Figs. 7(a) and 7(b) we show the spatial localization of the eigenvalues which are centered on the atoms of Figs. 3(b) and 3(c). Notice that both eigenvalues have become much more localized in the surface. These defects prove to be resistant to the usual passivation measures. We attempted to remove defects of this type by two methods: hydrogenation of the weak bond [2.75 Å in Fig. 3(c)] and “snipping” out the defective atom. In both cases, the localized states in question “migrated” to new sites and became even more localized. Simulated annealing for 0.2 ps at  $T \approx 1200$  K, followed by quenching, also failed to produce a model with fewer defects. At this time we are working on new treatments for these defects.

TABLE II. Coordination of Si atoms in an *a*-Si:H surface model. There are two fewer Si in the *a*-Si:H surface model due to the removal of two atoms during the passivation of a defect in the bulk region. The number of fourfold-coordinated atoms includes those with one and two H among the four neighbors. All H are singly coordinated.

No. of neighbors	No. of atoms
3	0
4	208
5	6

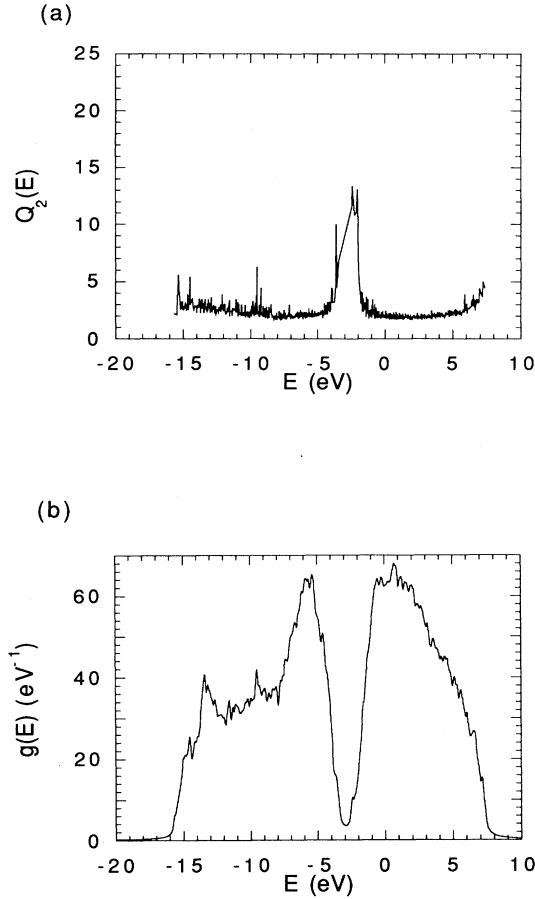


FIG. 6. (a) Charge localization for the hydrogen-terminated  $a$ -Si:H surface. There are fewer localized states near the Fermi energy, and the maximum value of  $Q_2(E)$  is less than that of the clean  $a$ -Si surface.  $Q_2(E) > 4$  is considered an electronic defect. (b) Electronic DOS for the hydrogen-terminated  $a$ -Si:H surface model.

We compute the electronic density of states (DOS) and plot it in Fig. 6(b). The electronic DOS is similar to that of the clean  $a$ -Si model. There is some increased weight in the conduction band, possibly due to the presence of additional Si-H bonds. As in Sec. III, we obtain values for  $E_c$  and  $E_v$ , and then estimate  $E_g$  from these. We find that  $E_v = -3.9$  eV and  $E_c = -1.8$  eV, which leads to  $E_g = 2.1$  eV. This is larger than the experimentally measured band gap values of 1.7–1.8 eV.<sup>2</sup>

## V. CONCLUSION

We have produced an *ab initio* model of a surface of  $a$ -Si:H. Beginning with an  $a$ -Si surface, we introduced H to passivate defects. We obtained a surface displaying a variety of atom coordinations. Due to the way in which the  $a$ -Si:H surface structure was generated, this

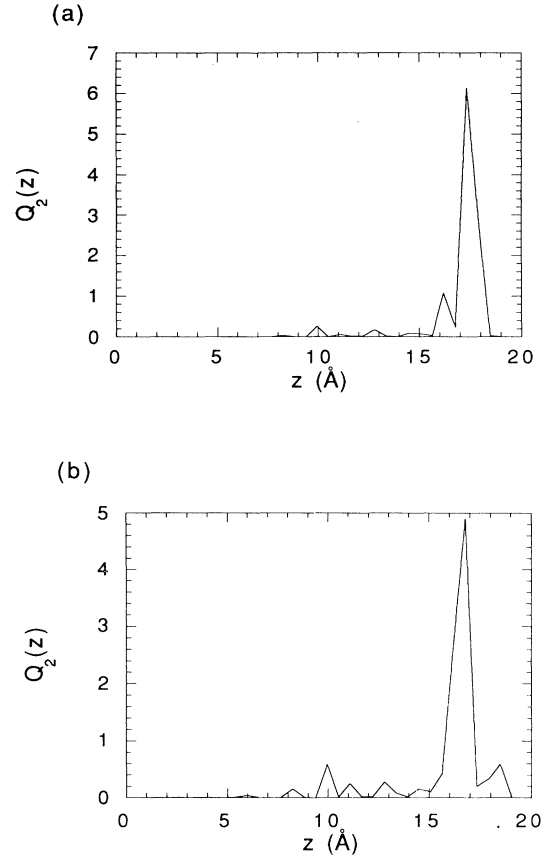


FIG. 7. (a) Spatial charge localization for the eigenvalue centered on atom 26 in the  $a$ -Si:H surface model. (b) Spatial charge localization for the eigenvalue centered upon atom 49 in the  $a$ -Si:H surface model.

model does not represent a typical  $a$ -Si:H surface during PACVD growth, since such a surface would have more  $\text{SiH}_2$  and  $\text{SiH}_3$  structures. However, it does reveal what some of the typical surface defects would be.

Charge localization is the way to infer that spectral defects exist. Various degrees of localization have been observed. On the question of correspondence between spectral and geometrical defects, we find that the link is a multifaceted one. There is a high probability that a threefold-coordinated atom will be the site of a localized eigenvalue, as the undercoordination of this atom signals the existence of a dangling bond. On the other hand, a fivefold-coordinated surface atom is not always the site of a localized eigenvalue. Furthermore, the simple criterion of coordination would not identify the distorted fourfold coordinated atoms as defects, although many of the spectral defects are found there.

With regard to issues of growth, we find the H-passivated dangling bond sites to be of great interest. There are several locations available to investigate the energetics of a dangling bond in various positions on the surface, as well as use molecular statics to study the chemisorption of  $\text{SiH}_3$  to the surface. This reaction is a key to the PACVD process.

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- <sup>22</sup> The fact that all atoms move slightly does not mean that our surfaces are just one side of a simple slab. The displacements of the top surface atoms are not similar in magnitude to those of the bottom surface atoms. This indicates that during the earlier relaxation with the bottom surface atoms fixed, the top surface atoms reached an arrangement that was relatively unaffected by the subsequent change in the bottom surface.
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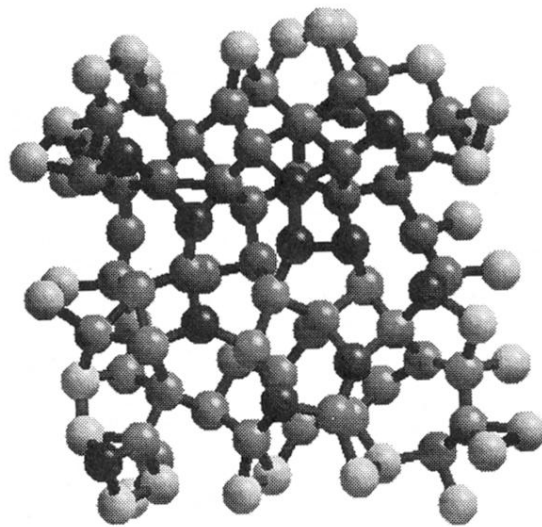


FIG. 1. Picture of a clean *a*-Si surface. The view is from above along the *z* axis. The periodic boundary conditions in the *x* and *y* directions have been used to show bonds between surface atoms and atoms in the image cells. The different shades of the atoms signify the following: light, atoms in neighboring cells; medium, fourfold- and fivefold-coordinated Si atoms; dark, threefold-coordinated atoms.



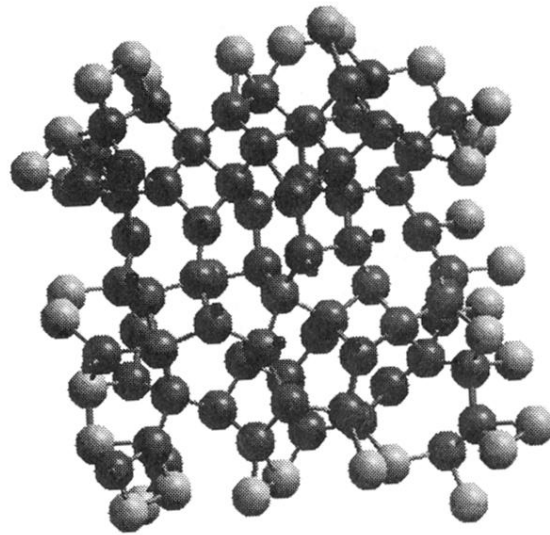


FIG. 5. Hydrogen-terminated  $a$ -Si:H surface. The shading of the Si atoms is the same as for the  $a$ -Si surface. There are no threefold-coordinated atoms on the surface. H atoms are in black.