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Tight-binding study of the electronic structure of amorphous silicon

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We have performed tight-binding calculations on a model of an amorphous silicon sample generated previously by a molecular-dynamics simulation employing the Stillinger-Weber potential. The sample consists of 588 atoms and contains a high density of floating-bond defects. Two tight-binding calculations are presented, one using the widely accepted Chadi parameters, which include only nearest-neighbor interactions, and the other using the parameters recently proposed by Allen, Broughton, and McMahan (ABM) [Phys. Rev. B **34**, 859 (1986)] for a nonorthogonal basis set. Comparison of the densities of states shows similar behavior in the valence band, but the electron density near a defect is less localized with the ABM parameters. It is also found that the projected density of states on the fivefold-coordinated atoms is very close to that on the fourfold-coordinated atoms, while the projected density of states on the threefold-coordinated atoms is distinctly different and has more states in the gap.

Currently, there is much interest in the study of amorphous silicon and, especially, in identification and characterization of the defects in this material. For years the predominant defect was believed to be the threefold-coordinated atom or dangling bond. Pantelides, though, has suggested that the fivefold-coordinated atom or floating bond is actually the major defect.[1,2] Different interpretations[3-5] of the electron-spin-resonance (ESR) spectra[6] give different conclusions as to which defect actually dominates. To model the structural properties, several molecular-dynamics (MD) simulations[7-12] have been done using model interatomic potentials. The resulting samples contain predominantly floating-bond defects in most cases. An exception is Ref. 9 in which the major defects in the amorphous silicon are associated with dangling bonds.

The electronic structure for these defects is of great interest and is useful in their characterization. Theoretical studies have been performed for clusters terminated by Bethe lattices[13,14] and for the aforementioned MD-generated sample[15] where dangling bonds were the major defect. Since the number of atoms involved is beyond the present capability of first-principles approaches, all these calculations used the tight-binding method.[16] These previous studies showed that the dangling-bond states are well localized at the central atom while the floating-bond states have amplitudes spread over the neighbors of the fivefold-coordinated atom. Based on the characteristics of the wave functions, it was suggested that the ESR hyperfine splitting is more likely due to the dangling-bond states.[13,15]

In this study we examine the electronic structure of a model amorphous-silicon sample generated by a recent MD simulation by Luedtke and Landman[8]. This sample differs from that used in Ref. 15 in several respects. It was obtained via direct slow cooling from the melt with the Stillinger-Weber interatomic potential.[17] The unit cell consists of 588 atoms, the largest number used in a simulation to date. The resulting sample contains far more floating than dangling bonds and the overall number of defects is quite large; about 22% of the 588 atoms are characterized as coordination defects. Among these defects, 121 are fivefold-coordinated atoms and only 3 are threefold coordinated.[18] It therefore allows us to study easily the effects on the electronic structure of a large number of floating-bond defects and their mutual interaction.

As noted, the tight-binding method is the only practical option at the present time to study the electronic structure of a system containing such a large number of atoms. To make systematic comparisons, we performed the calculation with two different sets of parameters for the *s* and *p* orbitals. The first set of parameters is the widely adopted one proposed by Chadi.[19] It includes only the first-nearest-neighbor interaction and a scaling factor (proportional to inverse-distance square) is used for different bond lengths. The second set of parameters, proposed by Allen, Broughton, and McMahan[20] (ABM), is derived by fitting the band structure of several different crystals and involves nonorthogonal overlap integrals. The overlap and energy integrals are represented by polynomials in terms of the atomic separation. The range of interaction goes up to the third-nearest neighbors in the diamond structure. For the calculation of amorphous silicon, we used a distance cutoff of 4.7 Å for these parameters. A supercell consisting of 588 atoms is constructed with periodic boundary conditions. There are four orbitals per atom, and the resulting Hamiltonian matrix is of the size 2352×2352. Since the energy dispersion is expected to be insignificant for this small Brillouin zone, only the eigenvalues at the Γ point are evaluated.

The calculated density of states (DOS) of the amorphous sample is shown in Figs. 1(a) and 1(b) for the two sets of parameters, respectively. The histogram is constructed by using an energy interval of 0.25 eV. It is well known that there are three peaks in the valence-band density of states of the crystal that correspond to, from lowest energy to highest, the *s* states, mixed *s*-*p* states, and *p* states. Results for the amorphous sample in Fig. 1 show that the first two peaks merge into a shoulder (at energies below -5 eV) and that the *p*-state peak (near -3 eV) is similar to that in the perfect crystal. This result agrees with what is observed in experiment[21] and also with previous calculations,[15] even though our sample has far more fivefold defects.

Although the overall features in the results of the two sets of parameters are similar, there are some visible differences in Figs. 1(a) and 1(b). One of them is the position of the *p* peak which differs by about 1 eV in two curves. Another difference is the number of states in the gap region. Since the number of defects in the sample is quite high, there are quite a few states in the gap. The ABM parameters, which include up to the third-nearest-neighbor interactions, give more states in the gap than the Chadi parameters, which include only the nearest-neighbor interactions. It is also worth mentioning that after summing over occupied bands, the number of electrons per atom can differ by as much as 10% for certain atoms when different sets of tight-binding parameters are used. Thus one has to be cautious in making quantitative comparisons for certain physical properties obtained from the tight-binding calculations.

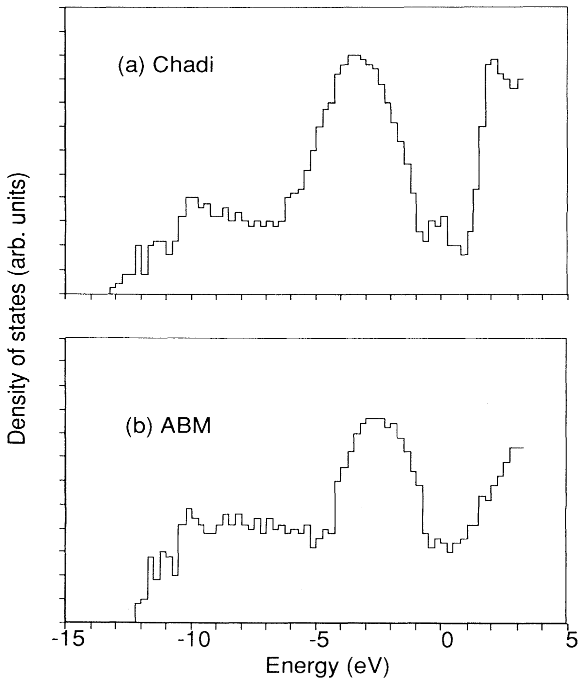

FIG. 1. Calculated density of states for the 588-atom amorphous-silicon sample using the (a) Chadi (Ref. 19) and (b) ABM (Ref. 20) tight-binding parameters. The energy zero is set at the top of the valence band in a perfect crystal.

In order to investigate the contribution from different defects, one needs to examine the projected density of states on atoms with different coordination numbers. The weighting is determined by the projection of the wave functions on individual atoms. The results using the ABM parameters are plotted in Fig. 2 for threefold-, fourfold-, and fivefold-coordinated atoms, respectively. [There are two curves in Fig. 2(b) which will be discussed later.] It is interesting to find that the curves in Figs. 2(b) and 2(c) are very similar, namely, the projected density of states on the fivefold-coordinated atoms is almost indistinguishable from that on the fourfold-coordinated atoms. This makes it difficult to isolate the contribution to the density of states from the fivefold defects. There exist states in the gap even for the fourfold-coordinated atoms because many of them have distorted tetrahedral bonds and some are neighbors of fivefold defects.

Since states associated with fivefold defects will be spread over the neighboring atoms, one should in fact examine the projected density of states on those neigh-

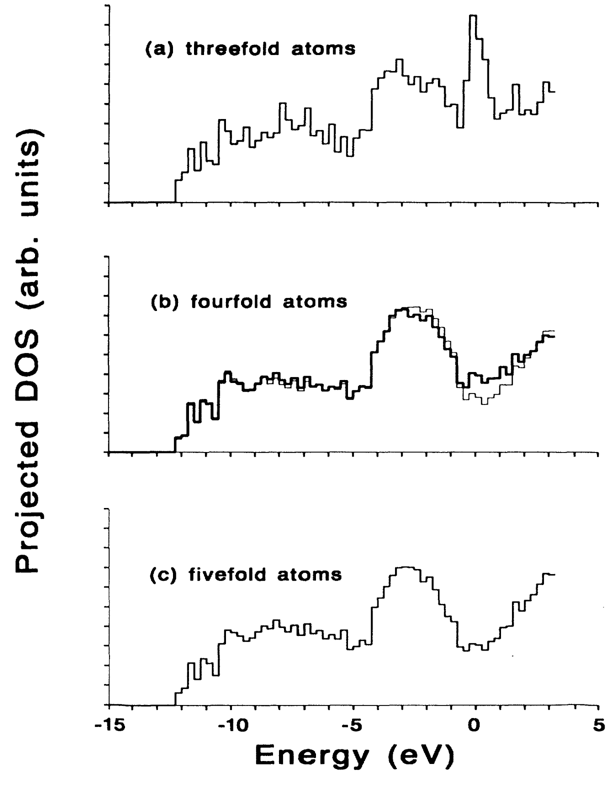

FIG. 2. Projected density of states for the amorphous sample on (a) threefold-, (b) fourfold-, and (c) fivefold-coordinated atoms using the ABM parameters (Ref. 20). For comparison, the curves have been normalized by the number of atoms involved. The thick line in (b) indicates the result for those fourfold-coordinated atoms which are neighbors of fivefold defects and the thin line for all fourfold-coordinated atoms.

boring atoms instead of the central ones. We have identified those atoms which are neighbors of isolated fivefold defects (i.e., all the neighbors of a fivefold defect which themselves are fourfold-coordinated atoms). The projected density of states for them is shown by the thick line in Fig. 2(b). Compared with the result for all of the fourfold-coordinated atoms [thin line in Fig. 2(b)], the effect of the fivefold defects can be observed: some states are pulled from the top of the valence bands and the bottom of the conduction bands into the gap. The effect, although visible in our analysis, is not dramatic. On the other hand, the projected density of states for the threefold-coordinated atoms [Fig. 2(a)] is significantly different from the other three curves in Fig. 2. A much larger fraction of states are within the gap region and the effect is much more prominent.

We examine next the electron density around defect atoms for individual states. For the dangling bonds, we find that the electron density is much more localized on the central atom (especially for states in and near the gap). Figure 3 shows a threefold-coordinated defect along with the electron densities for a state 0.2 eV below the Fermi level. This configuration is roughly tetrahedral with the angles and bond lengths marked in the figure. The electron population on each atom, calculated by using ABM parameters, is also shown. (The wave function of a single state is normalized in such a way that the average density is 1.0 per atom in the cell.) It is clear that the central atom has a much higher electron population, coming from the dangling bond. This is also found using Chadi's parameters and is consistent with previous studies.[13,15]

The electron densities for the floating bonds are especially interesting. For some eigenstates, those atoms that are the central atoms of a floating bond are more apt to have lower electron densities than one or two of their neighboring atoms which may have quite large electron densities. For some of our floating bonds the electron density is very large on those atoms which are further away (but still nearest neighbors) from the central atom. One configuration is shown in Fig. 4 for a state 0.2 eV above the Fermi level. The geometry involves a roughly collinear arrangement (similar to what is said to be the canonical arrangement[1]) with the three remaining atoms and the central atom close to being in a plane or cone roughly perpendicular to the axis of the nearly collinear atoms. The atoms involved in these collinear arrangements are usually the farthest or nearly farthest atoms from the central atom. Therefore, these collinear atoms (not including the central atom) typically have the largest electron densities of the particular eigenvalues that we looked at, although the absolute values could vary quite considerably in different atomic configurations.

When comparing the two different sets of parameters it is interesting to note that Chadi's parameters give much higher local electron densities than the ABM parameters,

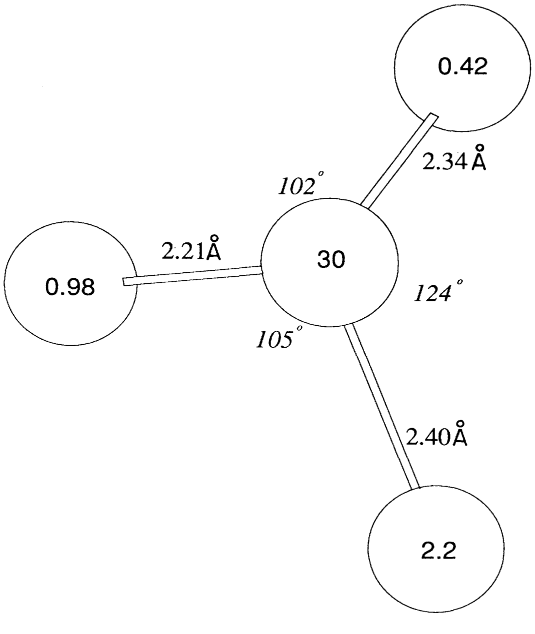

FIG. 3. Atomic configuration near a threefold-coordinated atom. The angles and bond lengths are marked. The electron electron population of a dangling-bond state (with an energy 0.2 eV below the Fermi level using the ABM parameters) is shown on each atom. The wave function is normalized in such a way that the average density is 1.0 per atom in the unit cell.

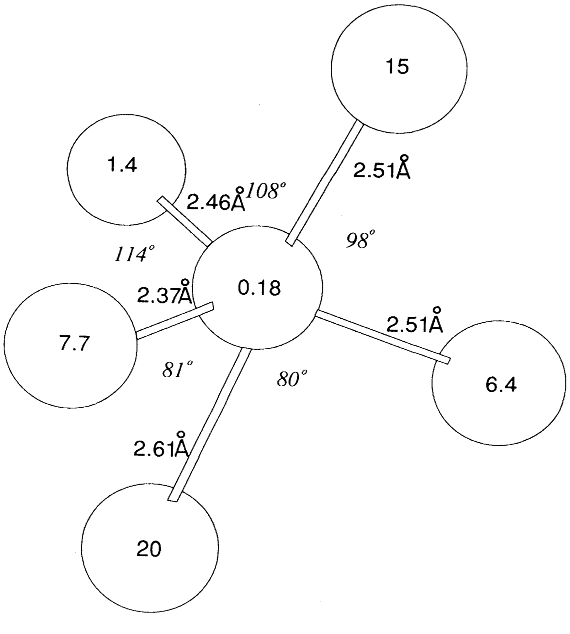

FIG. 4. Atomic configuration near a fivefold-coordinated atom. Selected angles and bond lengths are marked. The angle between the three almost-collinear atoms is 162°. The electron population of a floating-bond state (with an energy 0.2 eV above the Fermi level using the ABM parameters) is shown on each atom. The wave function is normalized in such a way that the average density is 1.0 per atom in the unit cell.

even though the latter gives more states in the gap. This is probably due to the fact that the ABM fitting includes up to third-nearest neighbors and, therefore, the electron densities are more spread out over these more distant neighbors.

In conclusion, we have performed calculations on the electronic structure of amorphous silicon using the tight-binding parameters proposed by Chadi (orthogonal basis) and by Allen, Broughton, and McMahan (nonorthogonal basis). The sample which we used in our study was previously generated by molecular-dynamics simulations[8] and contains mostly floating-bond defects. The density of states is fairly similar to that found in other calculations for samples with fewer defects and in which the defects are mostly dangling bonds. The projected density of states on the fivefold-coordinated atoms is almost identical to that on the fourfold-coordinated atoms, while the projected density of states on the threefold-coordinated atoms is significantly different and has more states in the gap. We also found that the charge distribution of a threefold-defect state is largely localized on the central atom and is localized on neighboring atoms for a fivefold-defect state; this is consistent with the results of previous studies. Comparison of the two sets of parameters shows that the Chadi's parameters give more-localized charge distribution than the ABM parameters.

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