Electronic structure of vacancies in amorphous silicon

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(Received 20 July 1994; revised manuscript received 9 November 1994)

The electronic structures of vacancies in amorphous silicon are studied by a tight-binding total-energy-minimization scheme. The most salient feature in the electronic structure is that deep gap states originating from the vacancies disappear in amorphous silicon while sustaining the vacant volume in most cases, unlike the vacancies in crystalline silicon. The origin of the disappearance of the deep gap states is explained by the relaxation of the neighboring atoms near the vacancy to enhance the strong $p_z$ bonding character which gives large bonding-antibonding splitting, and $sp^2 + p$ bonding character where $p$ states mostly contribute to the conduction bands.

The structure of amorphous silicon (a-Si) is generally believed to be a continuous random network with Si atoms being fourfold coordinated and covalently bonded. The well known point defects in a-Si are dangling and floating bonds, which are unique in amorphous materials only. The dangling (undercoordinated) bonds are considered to give rise to the deep localized gap states, which act as the traps in the electrical conductivity and the non-radiative recombination centers in the optical properties, whereas the floating (overcoordinated) bonds lead to less localized gap states. However, the experimental observation that the structural relaxation in irradiated a-Si is very similar to the annealing of point defects in crystalline silicon (c-Si) (Ref. 3) has raised the question of the existence of similar point defects in a-Si. The Mössbauer spectroscopy demonstrated that the point defects analogous to the crystal vacancy exist in the a-Si structure. The subsequent molecular dynamics (MD) simulational study using classical potential suggests that the vacancy in a-Si can be annihilated at room temperature, supporting the experimental observation of the annealing of the point defects. Presuming the existence of vacancies in the a-Si from such studies, the next question is as follows: What are the differences and similarities between vacancies of a-Si and those of c-Si? The vacancy can be considered as an agglomeration of four dangling bonds pointing toward the vacancy center. However, there is no guarantee that the vacancy in a-Si has the same physical properties as those in c-Si and even the dangling bonds in a-Si. We find that the most significant difference is that the vacancies in a-Si do not contribute to the deep gap states in the electronic density of states (EDOS) while retaining even the larger vacant volumes, in contrast to the vacancies in c-Si or with the dangling bonds in a-Si. The vacancy in a-Si in this sense belongs to a different category of point defects in a-Si.

In this paper, we address this issue using total-energy minimization scheme combined with MD method. We adopt Goodwin, Skinner, and Pettifor’s tight binding (GSP TB) total-energy scheme, which reproduces well the universal binding energy curves of various Si phases from the first principles calculations. The application of this scheme for analysis of various structures, such as point defects in c-Si (Ref. 7 and 8), a-Si (Ref. 9), and clusters, has proven to be very efficient and accurate in comparison to the experimental results.

In order to investigate the physical properties of defects in a-Si, one needs to take (i) a large a-Si network to minimize the interactions between the defects and (ii) a completely fourfold-coordinated random network, which can easily be tuned to investigate the effects from the chosen defects exclusively. We adopt a fourfold-coordinated random network with 216 Si atoms generated by Wooten, Winer, and Weaire (WWW) (Ref. 11), which describe well the structure factor of a-Si from the neutron scattering experiment. This network has fourfold covalent bonding locally but no long range order. The bond lengths and the bond angles are deviated from the tetrahedral structure. The average bond length is 2.37 Å and the bond angle is 109.5 ± 1°. To see how well our theoretical approach works at reproducing the EDOS, we calculate the EDOS of c-Si and the WWW a-Si network. The EDOS of c-Si from our TB total energy scheme is in excellent agreement with the first principles calculations as shown in Fig. 1(a). The EDOS from the WWW a-Si network also agree well with experiment. Since the GSP TB total-energy scheme reproduces well the universal binding energy curves of various c-Si phases from the first principles calculations, we believe that our theoretical approach can describe well not only the EDOS but also the general physical properties of a-Si. Although the conduction band is not well described by our model, the existence (or disappearance) of the gap states can still clearly be identified. The WWW model does not show
the gap states in the EDOS since they are all fourfold coordinated as shown in Fig. 1(b) and hence is suitable for the study of electronic structures of point defects exclusively. In this work, the original WWW model of 216 Si atoms is further relaxed via the dynamical annealing method at 300 K. The energy is lowered by 0.02 eV/atom.

The vacancy is created intentionally by simply removing a single atom in the complete network. Because various sites exist in the network, we choose individually weak (low formation energy), strong (high formation energy), and intermediate sites. We believe that these sites statistically sample the whole random network.

To achieve the ground state structures of vacancy, we performed microcanonical MD simulation for about 1 psec (1 timestep = $1.08 \times 10^{-18}$ sec) at room temperature so that all atoms are allowed to relax during this simulation time. The periodic boundary conditions are applied to the cubic supercell of 216 Si atoms (or 215 Si atoms for each single vacancy). The ground state structures are then obtained by a dynamical annealing with a quenching rate of $\sim 10^{15}$ K/sec. To make sure if the system is fully relaxed, we have tried 10.5 ps MD runs at higher temperatures but no significant differences are observed. We, therefore, believe that this period of simulation time is enough for the relaxation of the whole network. We have also tested the slower quenching rate to see if the system is in a metastable state or not, but obtained similar results. The choice of potential cutoff varies the formation energy slightly. We fix the potential cutoff $r_c = 3.2$ Å over the simulations so that the nearest neighbors are considered only during the relaxation.

The electronic density of states is one of the important physical properties in amorphous materials since it governs the optical and electrical properties. Figure 2 shows the typical EDOS of various vacancies near the energy gap where the EDOS is calculated by taking the sum over all eigenvalues of the system. When the vacancy is intentionally created, the EDOS (dashed line)

**FIG. 1.** The electronic density of states of (a) c-Si by pseudopotential calculations (Ref. 12) and our tight binding (TB) model and (b) a-Si by the experiment (Ref. 13) and (TB) our model.

**FIG. 2.** The typical electronic density of states (EDOS) near the energy band gap of various vacant sites. The reference (zero) energy is taken as a top valence band. The EDOS are broadened by the Gaussian with broadening factor 0.1 eV. The dotted, dashed, and solid lines indicate a complete network without the vacancy, single vacancy before relaxation, and after relaxation, respectively. The figure shows the EDOS of the vacancy of (a) a weak site, (b) a strong site. The V111 symbolizes the vacant site created by removing the 111th atom in the network.

**FIG. 3.** The local geometry of atoms near the vacant site (a) V111 and (b) V137 after relaxation. The white, black, and shaded balls indicate the vacant site, the nearest, and the second nearest neighbor atoms from the vacancy, respectively. The dotted line indicates the distances between the first nearest neighbor atoms after (before) relaxation. All units are in Å.
clearly illustrates the gap states in all cases. The EDOS of c-Si shows the gap states even after the full relaxation by MD and the subsequent dynamical annealing to the ground state structure. However, the deep gap states disappear in all cases of a-Si after the full relaxation. The energy gaps in some weak sites are even greater than that of complete network. The EDOS beyond the gap region shows no appreciable changes in all cases. We have calculated the EDOS of more sites but all show similar shapes. Figure 3 shows atomic configuration of local geometry of V111 and V137 sites after relaxation. The V111 site clearly illustrates that the distances between neighboring atoms near the vacancy become longer after relaxation, i.e., the vacant volume is expanded. The distances between neighboring atoms are slightly shorter but they still do not form strong bonds with each other.

The fact that the vacancy in a-Si does not contribute to the deep gap states, while sustaining the vacant volume, can be understood by introducing the s-p hybridization model. The detailed study of the correlation between bond angles and electronic bonding characters provides the physical intuition for the origin of the disappearance of the deep gap states.

When a defect is created in a crystal, the relaxation of neighboring atoms around the defect occurs so as to lower the total energy. This relaxation occurs toward a prevalent direction between the tendencies of (i) preserving the symmetry of the system and (ii) lowering the symmetry of the system (Jahn-Teller distortion). The electronic interaction energy depends on, not only the relative distances, but also the relative angles between neighbors. The electronic structure of the neighboring atoms near the vacancy can be determined from the bond angles between backbonded atoms. In c-Si without defect, the bond angles are 109.5°, forming sp³ bondings. If the bond angle with defect is greater than 109.5°, i.e., the bond angle gets close to 120°, the electron has sp² bonding. If the angle gets close to 90°, the electron has p³ or pπ bonding.

In the a-Si network with vacancy, no high symmetry exists in the network, unlike the c-Si and, therefore, no Jahn-Teller distortion has occurred. Instead, the relaxation occurs toward a direction of recovering the symmetry. The bond angles of neighboring atoms near the vacancy, after relaxation, change to a direction of (i) decreasing the bond angles (type I) and (ii) increasing the bond angles (type II). In the V111 site, the bond angles of atom 106 with backbonded atoms decrease an average of 7° after relaxation (type I). To see the effect of relaxation of bond angles, we calculate the local density of states (LDOS), which can be calculated by projecting the EDOS to each specification. As shown in Fig. 4(a), the gap states are shifted to the top valence states by this effect. On the other hand, the bond angles of atom 116 with backbonded atoms increase an average of 12° after relaxation (type II). This effect shifts the gap states to the conduction bands as shown in Fig. 4(b). In both cases the effect of bonding-antibonding splitting becomes larger, shifting the gap states to each band tail. This effect can also be observed in the V137 site. The bond angles of atom 62, with backbonded atoms, are decreased by 21° after relaxation (type I) and, therefore, the top valence bands are developed, as shown in Fig. 4(c). The bond angles of atom 108 with backbonded atoms are increased by 8° after relaxation (type II), which contributes to the conduction bands, as shown in Fig. 4(d).

The peak position with the energy gap of the LDOS before relaxation depends on the average bond angles with backbonded atoms. If the bond angle is greater than 109.5°, the peak position resides near the conduction band. If it is less than 109.5°, the peak resides near the valence band. The larger deviation from the tetrahedral angle (109.5°) shifts the peak position closer to each band. For instance, the atom 106 of the V111 site has a smaller angle by 4° in average, compared to 109.5°. We, therefore, see the peak position near the valence band as seen in Fig. 4(a). On the other hand, the atom 138 of V137 site has a larger angle by 2° in average and, hence, we see the peak position near the conduction band. Table I shows the summary of two types of relaxations.

The existence of two types of bond angle relaxations observed in a-Si with the vacancy is similar to the formation of an asymmetric dimerization on Si (001) surface. It has been reported that the total energy is lowered by asymmetric dimerization, i.e., the bonding of the down atom changes into sp² + p bonding, where the p state mostly contributes to the unoccupied state, and the bonding of the up atom changes into p³ or pπ bonding.

TABLE I. Types of relaxation of bond angles between the neighboring atoms near the vacancy and the backbonded atoms. Δθ = (θb − θa), where θa(θb) is the average of the bond angles after (before) relaxation.

<table>
<thead>
<tr>
<th>Type</th>
<th>Bonding state</th>
<th>Occupancy</th>
</tr>
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<tbody>
<tr>
<td>I</td>
<td>p³</td>
<td>occupied</td>
</tr>
<tr>
<td>II</td>
<td>sp² + p</td>
<td>unoccupied</td>
</tr>
</tbody>
</table>
bonding, which mostly contributes to the occupied state. The bond angle of the up atom with the neighboring atom is 91.5°, close to 90°, and that of the down atom is 115°, close to 120°. These observations are also in good agreement with Saito and Oshiyama’s s-p hybridization model.

In summary, we have calculated the electronic structure of the vacancy in a-Si. The most significant difference of vacancies between a-Si and c-Si is the disappearance of the deep gap states in a-Si. This is explained by the relaxation of the bond angles between neighboring atoms near the vacancy and those backbonded atoms. We find two types of relaxations: (i) decreasing the bond angles (type I), which contributes to the valence bands and (ii) increasing the bond angles (type II), which contributes to the conduction bands. This relaxation increases bonding-antibonding splitting such that the deep gap states are removed.

We thank G. D. Watkins and M. Saito for helpful discussions. We thank J. Jang for encouraging us to continue this work. This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the Semiconductor Physics Research Center (SPRC) at Jeonbuk National University.