Supplementary material for: Electronic Structure and Localized States in Amorphous Si and Hydrogenated Amorphous Si

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Electronic properties of a-Si and a-Si:H modeled with different supercells

To ensure that the presented results in the paper does not depend on a specific supercell, two other sample supercells, one containing 64 Si atoms (a-Si64) and another containing 216 Si atoms (a-Si216), are tested as the starting structure for DFT calculations. Following is our results obtained from these supercell samples.

The a-Si64 supercell sample contains two DBs (labeled here as Si#59 and Si#20) and no FBs. Our structural analysis shows that when the first H atom is added to the a-Si64 supercell, the most stable configuration of a-Si64H corresponds to a H atom bonded to Si#46, not to the dangling bond Si#59 or Si#20. The position of Si#46 in the a-Si structure is illustrated in Figure 1. Although the Si#46 atom does not have a dangling bond, it is under a significant ring strain (RS) since it's shared between two unstable 4-fold rings. We also find that the H atom bonded to Si#46 results in removing one of the DB (Si#20) present in the supercell , which is spatially far from the H position in the supercell. With continued insertion of H atoms to the supercell, we found again a sensitivity of Si atoms under bond or ring strain to hydrogen addition. In almost all the cases, in the most stable configurations, H atoms add to the Si atoms under either bond length strain or ring strain.



FIG. 1. The position of a) Si#46 (blue colored) and Si#47 (red colored) and b) Si#20 (blue colored) and Si#53 (red colored) in a-Si structure.

Figure 2 illustrates the calculated electronic density of states (EDOS) plot of the a-Si64 and a-Si64:H close to the bandgap. Looking in detail at the EDOS, it's obvious that adding H atoms to the a-Si64 structure noticeably decrease the mid-gap state density and increase the band gap. Since H atoms mostly attach to strained bonds rather than DB, this mid-gap state reduction and band gap increase is attributed to removing strained bonds rather that passivating DBs.



FIG. 2. Calculated EDOS of a-Si:H close to the band gap for different H concentrations 0% (a-Si64), 3.03% (a-Si64H2), 5.88% (a-Si64H4), 10.0% (a-Si64H6), and 11.1% (a-Si64H8).

The contribution of each atom (IPR_k) in the localization of all the electronic states in the mobility gap (6.0-8.0 eV) of a-Si64 was also calculated. Figure 3 shows the IPR_k values for each atom in the a-Si64 supercell. As indicated, Si#46 and Si#47 (Si atoms with strained bonds) have very large contributions, almost as large as Si#20 and Si#59 (Si atoms with DBs), in the localization of all the electronic states within the mobility gap of a-Si.



FIG. 3. The relative contribution of each atom in the orbital localization of a-Si64. DB and SB stand for dangling bond and stained bond, respectively.

For the case of a-Si216 supercell, we found three dangling bonds (labeled here as Si#9, Si#57 and Si#158, illustrated in Figure 4 below) and three floating bonds (FBs).



FIG. 4. The position of a) Si#57 b) Si#158 and c) Si#9 atoms (illustrated with red color) in the a-Si216 supercell and the bond lengths associated with them. All the lengths are in angstroms.

Once a H atom is inserted to this supercell, the H atom is traditionally expected to passivate one of these dangling bonds in the most stable configuration of a-Si216H. However, our calculations show that the most stable configuration of a-Si216H corresponds to a H atom bonded to a Si atom (illustrated in Figure 5a) under both bond angle and bond length strain, not to one of the dangling bonds. We found that binding H atom to this Si atom results in removing one of the FBs which is spatially separated from the H position in the supercell. While the number of dangling bonds remain the same but their positions in the a-Si216 supercell change (Figure 7). We also examined the atomic structure of a-Si:H, when a more H atoms are inserted into the a-Si216H supercell. We found again a sensitivity of Si atoms under bond angle or bond length strain to hydrogen addition. Figure 5b, 5c, 5d, 5e, and 5f show the Si atoms which were the target of H attack with inserting a second, third, forth, fifth and sixth H atom, respectively, to the supercell. Only for the case of inserting the sixth H atom, the H atom is bonded to a Si atom with a dangling bond. In all those cases, we observe a change in the number of dangling bonds and floating bonds in the supercell although H atom bonds to Si atoms with strained bonds.



FIG. 5. The position of Si atoms (red colored) in a-Si structure involved in H addition in a-Si:H with the H atomic percent of a) 0% (a-Si216), b) 0.46% (a-Si216H), c) 0.92% (a-Si216H2), d) 1.37% (a-Si216H3), e) 1.82% (a-Si216H4), and f) 2.26% (a-Si216H5).

Figure. 6 shows the calculated electronic density of states plot of the a-Si216 and a-Si216:H close to the band gap. Consistent with the obtained results from previous supercells, we observe that midgap state density decrease and bandgap increase with H addition to the strained bonds in the a-Si216 supercell.



FIG. 6. Calculated EDOS of a-Si216 close to the band gap for different H concentrations 0% (a-Si216), 0.92% (a-Si216H2), 1.82% (a-Si216H4), and 2.70% (a-Si216H6).

Figure 7 shows the IPR_k values for a-Si216 and a-Si216:H with different hydrogen concentration. As seen from Figure 7a, in addition to DBs, SBs also have significant contributions in the orbital localization of a-Si216 and a-Si216:H. The two strongest peaks are related to one of the DBs (Si#57) out of three DBs (Si#57, Si#158, and Si#9) present in the a-Si216 supercell. Although the assumption is that after a certain bond length cutoff there is no bond between two Si atoms, but as clearly seen from Figure 4, the longer DB bond length of Si#57 might be the source of this higher orbital localization.

Figure 7b, 7c, and 7d are showing the IPR_k values after H addition to the a-Si supercell. It's obvious that regardless of the H position in the supercell, the contribution of all Si atoms in the orbital localization decreases as the H concentration increases in a-Si:H. As shown before, in almost all the most stable configurations of a-Si:H supercells, H atoms were bonded to Si atoms with strained bonds rather DBs, however this interaction still leads to a reduction in the orbital localization caused by the DBs, which are very far from the H position.

For further improving our finding in the importance of strain in creating midgap states and hydrogenation processes, we created several different a-Si216 supercells using MD simulation with different quenching rates. Figure 8 shows the EDOS of three sample supercells with their excess energy. From this Figure, we observe that although the number of dangling bonds in the case of the lowest strained structure is more than the number of dangling bonds in the case of the highest strained structure, but the density of midgap states is significantly less for the lowest strain structure.



FIG. 7. The relative contribution of each atom in the orbital localization of the modeled a-Si:H supercell with a) 0% (a-Si216), b) 0.92% (a-Si216H2), c) 1.82% (a-Si216H4), d) 2.70% (a-Si216H6) H atomic concentration.



FIG. 8. Calculated EDOS, close to the band gap of a) different a-Si samples with different strains.