Hydrogen-Acceptor Pairs in Silicon

In a recent Letter, Assali and Leite (AL)[1] propose a model for the structure of a hydrogen-boron pair in silicon and the concomitant loss of shallow-acceptor activity. Using the MS-$X\alpha$ cluster method, they explore single-particle and total energies as functions of H displacement from the T_d interstitial position towards the substitutional B.

In this Comment, we would like to point out recent theoretical and experimental studies of the H-B pair which were not addressed in the Letter of AL. These results and further calculations that we report here strongly suggest that the AL model for the H-B pair (B_sH_i) is not the stable, minimum-energy configuration.

We have previously reported[2,3] both MS-$X\alpha$[4] and modified neglect of diatomic overlap (MNDO)[5] computational results for the H-B pair. Using the MNDO-cluster method, we found that, with B on center, H did not remain along the line explored by AL.[2,3] Furthermore, allowing both the H and B to relax, we found that the interstitial H moved into a position between the B and one of its bonding Si neighbors producing a Si—H bond, while the B moved off center in the opposite direction to attain threefold coordination with the remaining silicons.

This acceptor-deactivating configuration was originally suggested by Pankove and co-workers.[6] Here, the B and H interact with each other only weakly; we have effectively a SiH--BSi$_3$ system. This can be contrasted with the AL model, which has an interstitial H interacting primarily with on-center substitutional B (a H—BSi$_4$ system).

Further support for the Pankove model comes from recent infrared studies[7,8] and supporting theoretical work.[3] In the experimental studies, an 1870-cm^{-1} absorption was correlated with the H-B pair defect. The Pankove (SiH--BSi$_3$) model was favored since the observed H vibrational frequency was consistent with a Si—H bond. This conclusion was subsequently supported by our MNDO computations, where we calculated a value of 1880 cm^{-1}.[3] Any model which would involve H vibrations in a B—H bond was rejected by Pankove since it would be expected to produce an absorption at ~ 2560 cm^{-1}.

We have done follow-up MNDO calculations using a hydrogen-terminated version of the AL cluster (BHSi$_{10}$H$_{18}$ with frozen silicons). Exploring first the AL configuration, we find a minimum when H is 1.19 Å along the interstitial direction from an on-center B (compare with 1.8 Å from Fig. 2 of AL). For this configuration, we calculate a 2590-cm^{-1} H vibration,[9] which is consistent with the argument by Pankove and co-workers.

We also calculate the total energies for the Pankove and AL orientations of the B-to-H pair axis {[111] vs [11$\bar{1}$], respectively, in a (1$\bar{1}$0) plane}. For each orientation, the total energy is minimized with respect to independent H and B motion along the line. We find that the [111] Pankove orientation is lower in energy by 1.3 eV. Therefore, the AL minimum is a saddle point according to our calculations.

As a final, related comment, we note that the acceptor-deactivating configuration suggested by AL has been proposed and well studied for the Li-B pair in silicon.[10] In fact, we find in using the MNDO method that it is the [11$\bar{1}$] AL configuration of the Li-B pair which is favored over the [111] Pankove orientation by 1.9 eV. This affinity of Li to the interstitial site is consistent with our earlier studies.[11]

In summary, we suggest that the potential-energy surface explored by AL was too limited. This we conclude on the basis of our MNDO calculations which indicate that (i) the AL configuration is a saddle point, with the Pankove configuration producing the true minimum, and (ii) the computed H vibrational frequency is in agreement with recent infrared studies for the Pankove model, but not for the AL model.

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