## Theoretical Studies of Structure and Doping of Hydrogenated Amorphous Silicon

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## ABSTRACT

In a-Si:H, large concentrations of B or P (of order 1%) are required to dope the material, suggesting that doping mechanisms are very different than for the crystal for which much smaller concentrations are required. In this paper, we report simulations on B and P introduced into realistic models of a-Si:H and a-Si, with concentrations ranging from 1.6% to 12.5% of B or P in the amorphous host. The results indicate that tetrahedral B and P are effective doping configurations in a-Si, but high impurity concentrations introduce many defect states. For a-Si:H, we report that both B(3,1) and P(3,1) (B or P atom bonded with three Si atoms and one H atom) are effective doping configurations. We investigate H passivation in both cases. For both B and P, there exists a "hydrogen poison range" of order 6 Å for which H in a bond-center site can suppress doping. For B doping, nearby H prefers to stay at the bond-center of Si-Si, leaves B four-fold and neutralizes the doping configuration; for P doping, nearby H spoils the doping by inducing a reconstruction rendering initially tetrahedral P three-fold.

# **INTRODUCTION**

By introducing B or P, a-Si:H may be doped either n-type or p-type [1], a point of profound technological importance. In c-Si, doping has been extensively studied. Because of translational invariance, impurities are compelled to have the same local tetrahedral environment as Si. According to the 8-N rule, B atoms create a hole when they have T<sub>d</sub> symmetry, and P similarly donate an electron. The doping efficiency is almost 100%. In c-Si:H, H atoms passivate doping by relaxing strain, and rendering B or P doping-inactive by enabling the impurities to become three-fold [1]. In this short paper, we make no pretense of properly reviewing the substantial literature on the subject and recommend the book of Street[1] as a suitable introduction.

In a-Si or a-Si:H, the absence of a unique atomic environment leads to site-dependent doping, as seen in studies with low concentration of Boron [2]. However, theoretical studies on P doping and high concentration of B are still needed. Early experiments show a very low doping efficiency in a-Si:H, with a doping efficiency rollover observed in experiment when impurity density is around 1% [1,3]. NMR [4] shows that, for B doping, 40% of the B has a nearby H at 1.6 Å; for P doping, 50% of P has a H at 2.6 Å. Boyce and Ready have conjectured that the sluggish doping may be due to H passivation [5]. But the atomistic mechanism of H passivation in doped a-Si:H is unclear.

In this paper, we report molecular dynamic simulations on B and P doped a-Si and a-Si:H, focusing on the impurity geometry and associated electronic structure. For a-Si, we report the electronic density of states (EDOS) for various impurity concentrations based on substitutional doping. We seek to determine the effective doping and non-doping configurations. For a-Si:H, we focus primarily on describing the H passivation mechanisms for the system with 1.6%

impurities. By manually placing H in the models, and allowing the system to relax, we are able to investigate energetically preferred impurity positions and explore consequent electronic structure. We should point out that this work leaves many stones unturned; the discussion of doping efficiency versus dopant density in a-Si:H, the thermal stability of effective doping configuration, and dopant diffusion in a-Si:H are not included here. We will report more details of those important topics in a future paper.

## THEORY

All calculations were performed using the plane wave LDA code VASP with ultrasoft pseudopotentials and the local density approximation [6]. A previously generated defect-free 64atom a-Si model was used as the initial configuration. B or P atoms were introduced into the network by substituting for Si atoms. Conjugate-gradient relaxations were performed at constant volume. We obtained relaxed 1.6%, 3.1%, 7.8% and 12.5% B or P doped a-Si models. To study H passivation in B- or P-doped a-Si:H, we introduced H atoms at particular sites of the 1.6% Bor P-doped a-Si models with various distances from impurities.

### DISCUSSION



Fig. 1 Electronic density of states (EDOS) (a) a-Si. (b) a-Si:H. The Fermi level is at 0eV.

We first present the electronic density of states of a 64-atom a-Si model and a 70-atom a-Si:H model with 8.5% H in Fig. 1. Both a-Si and a-Si:H models exhibit gaps unsullied by defect states. In the following, we first discuss B- and P-doped a-Si with impurity concentrations from 1.6% to 12.5%. Then, we investigate the mechanism of H passivation in both systems.

## **Boron doped a-Si**

We plot the EDOS of seven B-doped models [configuration (1)-(7)] in Fig. 2. Overall, when B atoms are introduced substitutionally into the network, the Fermi level shifts toward the valence edge, signaling doping. In configuration (1), (2), (4) and (7), all B atoms are four-fold and prefer to form three shorter bonds and one longer bond with Si. As the concentration increases, more valence tail states are formed, and states move into the gap. Where B dimers or clusters are concerned, it seems that B-B bonds won't impact the doping as long as B atoms are

four-fold as shown in configuration (3). However, when more B dimers or clusters are formed, additional defect states appear near the conduction tail, and they clutter the gap, as shown in configuration (5) and (6). Those defect states are associated with under- and over-coordinated Si atoms.



**Fig. 2** Boron doped a-Si with different impurity concentrations. (a) 1.6% (b) 3.1% (c) 7.8% (d) 12.5%. In configuration (1), (2), (4) and (7), all B are bonded with four Si atoms. One B dimer is formed in configuration (3). Two B dimmers exist in configuration (5) and one B<sub>4</sub> cluster formed in configuration (6). The Fermi level is at 0 eV.

We conclude that tetrahedral B makes the Fermi level shift from mid-gap into the valence band tail and effectively dopes the system. However, as B concentration increase, more valence tail states are formed. B clusters may introduce tail and mid-gap states, which impacts the doping and surely transport.

#### Phosphorus doped a-Si

We plot the EDOS of eight models [(1)-(8)] of P-doped a-Si in Fig. 3. We found that tetrahedral P forms deep donor states and the Fermi level shifts toward the conduction band tail. As P concentration increases, more defect states appear, and the gap closes (configurations (1), (2), (5), and (8)). P dimers and clusters dope the system so long as all P are four-fold

(Configuration (3),(5)), but they also lead to defects which give rise to tail states. If P atoms are three-fold (configuration (4)), the configuration is non-doping.



**Fig. 3** Phosphorus doped a-Si with different P concentration. (a) 1.6% (b) 3.1% (c) 7.8% (d) 12.5%. In (b) configuration (4) is a non-doping configuration. The Fermi level is at 0eV.

Thus, for P doping, tetrahedral P dopes the system by shifting the Fermi level into the conduction tail. As for B doping, as concentration increases, more defect states move into gap. Three-fold P is a non-doping configuration.

### H passivation in B doped a-Si:H

We next report that B (3,1) (B atoms bonded with three Si atoms and one H atom) is an effective doping configuration. The structural evolution and corresponding EDOS is plotted in Fig. 4 and Fig. 5.

H is initially attached to a B atom and makes B form a metastable unit B(4,1) as in Fig. 4 (a). After relaxation, H breaks one Si-B bond forming a B(3,1) structure and leaves one Si DB, as in Fig. 4 (b). The EDOS of this configuration reveals that the Fermi level shifts back into gap. One mid-gap state forms due to the Si DB. However, if another H passivates the Si DB, as in Fig.4 (c), the Fermi level shifts into valence band tail once again and the mid-gap state disappears. Thus, we conclude that the B(3,1) without a Si DB is an effective doping conformation. This confirms the simulation results reported in Ref [5].



**Fig. 4** H passivation at B site. (a) H initially bonds with B and B forms B(4,1) structure. (b) After relaxation, B becomes B(3,1) with a vestigial Si DB. (c) Another H passivates the Si DB. The cyan (light, big) atom is B, blue(dark, big) atoms are Si and white(light, small) atom is H.



**Fig. 5** EDOS comparison of configurations during H passivation. The black (dashed) line shows the original B doped a-Si. The red (solid) line shows the EDOS of B(3,1) and one Si DB. The blue (dotted) line shows the EDOS when Si DB is passivated by another H. The Fermi level is at 0eV.

Next, we show that H prefers to stay at the bond center (BC) when near a B atom and this BC H suppresses the doping. We show two cases of H passivation with different H-B distances in Fig. 6. The top panel (a) of Fig. 6 shows the situation in which H is initially bonded to a Si neighbor of the B atom. After relaxation, H breaks the Si-Si bond and stays at the BC forming a B-Si-H-Si structure, the top panel [6(b)]. The EDOS shows that the Fermi level shifts back from the valence tail into the gap, indicating that the BC H kills the doping. The bottom panel of Fig. 6 shows similar passivation with H bonded to a second neighbor Si of B atom and finally forming a B-Si-Si-H-Si structure. The EDOS of the B-Si-Si-H-Si structure shows that it is also a non-doping configuration. These results indicate that BC H sufficiently near a B atom will neutralize the doping. Notice that, in all cases, there is no reconstruction of B atoms -- which are still 4-fold

after relaxation. There is no Si DB left in the network and no defect states in the gap. Further calculations indicate that there is an "H kill range" for BC H passivation. If the distance between H and B is beyond about 6.0 Å, the passivation seems to not occur.



**Fig. 6** BC H passivates the doping. Top panel is the situation for B-Si-H-Si; bottom panel is the case for B-Si-Si-H-Si. The EDOS show the comparison between B doped a-Si and the final relaxation result when BC H exists in the network. The Fermi level is at 0eV.

The mechanism of this BC H passivation at low B concentration may be related to charge interactions. In Ref [2], at low concentration of B, it is confirmed that holes could be trapped at strained Si-Si bond centers. Thus, the H may compensate by staying at the BC and killing the doping structure. Another calculation in a-Si:H also confirm this. In a-Si:H, the Si (4,1) structure (Si bonded with four Si and one H) is stable. However, if one electron is removed from the system, H tends to break a Si-Si bond and occupy the BC position. Considering the "H poisoning range", it may be related to the exciton radius [7], which is about 5.9 Å in a-Si.

## H passivation in P doped a-Si:H

In analogy with H passivation in B doped a-Si:H, we investigate H passivation in Pdoped a-Si:H. We first report that P(3,1) is an effective doping configuration. The simulation is shown in Fig.7 and Fig. 8. H is originally bonded to P forming a P(4,1) metastable structure. After relaxation, a P-Si bond breaks. H sticks to the P, forming a P(3,1) structure with a Si DB. The corresponding EDOS indicates that the deep donor state disappears, the Fermi level shifts back to the gap, and there is one mid-gap state formed (due to the Si DB). The configuration becomes non-doping. However, if another H passivates the Si DB as shown in Fig.7 (c), the Fermi level again shifts to the conduction tail. Thus, we conclude that P(3,1) is an effective doping structure, but the Si DB in the network may eliminate the doping.



**Fig.7** H passivation at P site. (a) H bond with P forming a P(4,1) structure. (b) H breaks one P-Si bond and makes P form P(3,1) with one Si DB. (c) another H passivates the Si DB. Green (light, big) atom is P. Blue(dark, big) atom is Si. White (small) atoms is H.



**Fig. 8** EDOS: comparison of configurations during H passivation. Black (dashed) line is P doped a-Si. Red (solid) line is P(3,1) with one Si DB. Blue (dotted) line is the P(3,1) with another H passivate the Si DB. The Fermi level is at 0eV.

We then show two cases of H passivation in P doped a-Si:H in Fig.9. Unlike H passivation in B-doped a-Si:H, H in this network does not prefer BC position. In the top panel (a) of Fig.9, H is originally at BC of a P-Si bond and makes a P(3,1) structure. However, after relaxation, the H-P bond ruptures, the H bonds with Si, and P becomes three-fold. The EDOS becomes non-doping as the deep donor state disappears and the Fermi level is now in the gap. The bottom panel of Fig. 9 shows another case. H is initially at a bond center of Si-Si and forms a P-Si-H-Si structure. After relaxation, the network reconstructs as P becomes three-fold and H sticks to a Si DB. The doping is rendered inactive. Notice that there are no defect states in the EDOS of final configuration. Further calculations show that again there exists an "H kill range" of ~ 6.0 Å. When H is sufficiently near a P site in a BC configuration, the network will reconstruct so that P becomes three-fold, H sticks to Si DB, and neutralizes the doping structure.



**Fig. 9** H passivation in P doped a-Si:H. Top panel, H originally formed P-H-Si; bottom panel, H originally formed p-Si-H-Si. After relaxation, in both cases, P becomes three fold and non-doping configurations. Green (light, big) atom is P. Blue(dark, big) atom is Si. White (light, small) atom is H. The Fermi level is at 0eV.

Unlike H passivation for B, H does not prefer the BC position, instead it prefers to bond with Si. This result is consistent with NMR, which implies that P often has an H neighbor around 2.6 Å away (*not* the first neighbor distance).

## CONCLUSIONS

Tetrahedral B and P dope the system, but uniformly distributed high concentrations of impurities greatly reduce the gap. Clusters also create defect states in the gap. Strongly supporting experimental conjectures[4], H passivation is a key to understanding doping efficiency. We also make it clear that the basic mechanism of doping is quite different from the crystal and we can gauge success not by the appearance of a shallow level, but my monitoring the position of the Fermi level. The configurations B(3,1), P(3,1), Si(3,1) are effective doping states. There exists an "H kill range": for B doping: when BC H sufficiently is near B, H breaks the bond and stays at the bond center; for P doping, H atoms bond to Si and induce a reconstruction leaving P three-fold and thus electronically inert.

Most calculations in this paper are based on direct relaxations. We are currently performing long MD runs to study the thermal stability of B, P tetrahedral structure in a-Si, the interaction between H and impurities at high temperatures in a-Si:H, and H passivation in a-Si:H

with high concentrations of impurities distributed in various ways. Another topic for future study would be to decipher the importance of charge states on the doping and defect equilibrium. The key finding of this paper is that BC H has a powerful and negative effect on doping a-Si:H both for B and P impurities, and in the case of P tends to convert tetrahedral P into trigonal P, resulting in suppression of doping. For B too, H suppresses doping, though it seems less able to induce a trigonal reconstruction at the B site.

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