

Theory of phosphorus doping in *a*-Si:H

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(Received 15 April 1998)

For a long time the rather low doping efficiency of P and B in *a*-Si:H has been explained by the argument that almost all of both is incorporated into threefold-coordinated sites, and that both are inert or nondoping in this configuration. Recently, using *ab initio* molecular dynamics, the energetics and electronic structure (doping) consequences of B incorporation into *a*-Si:H both with and without H passivation were studied. This work showed that the conventional view was in error and that the low doping efficiency in B is primarily due to H passivation. In this paper we similarly study P incorporation on *a*-Si:H both with and without passivation. We obtain quantitative results on the energetics and electronic structure of P atoms in *a*-Si:H. In this case, the results do support the conventional view. Thus P and B act very differently in *a*-Si:H. However, we also find that the P-H complexes that passivate P in crystalline Si are not even metastable in *a*-Si:H. [S0163-1829(98)08035-7]

I. INTRODUCTION

It is well known that the doping efficiency of both P and B in *a*-Si:H is quite low.¹ The doping efficiencies are about 10% at low concentrations, and fall off as the concentrations rise. Further, effective doping efficiencies are considerably less because of the filling of band tail and defect states. Earlier this low doping efficiency was nearly universally attributed to the belief that almost all of both P and B was incorporated into threefold-coordinated sites, and that they were inert or nondoping in this configuration. This is in marked contrast to the situation for *c*-Si, where the doping efficiencies of P and B are both virtually 100%. In recent work² we showed that this picture was in error for B, and that it is energetically very unfavorable for B to sit at a threefold-coordinated site in *a*-Si:H, and that even in such sites the B “impurity” acts as a dangling bond. For these reasons, we concluded that most B in *a*-Si:H is incorporated into B-H complexes, and thus that B is passivated very much like it is in crystalline Si.

The above results have motivated us to perform a similar theoretical study of the incorporation of P in *a*-Si:H. Although B is known as an “odd” atom in many ways, one might still expect P and B to act similarly in *a*-Si:H. Further, H passivation of P in crystalline Si is only marginally metastable, and the energetics and stability of the configuration is not clear.^{3,4} For these reasons, and because the energetics of P incorporation in *a*-Si:H are of interest and use, we have extended our previous work to the incorporation of P in *a*-Si:H. We have performed extensive molecular-dynamics (MD) calculations on the incorporation of P into *a*-Si:H networks, and have studied both the energetics and electronic (doping) consequences of P incorporated into the network both with and without H passivation. Our studies support the traditional view that threefold-coordinated P is responsible for the low doping efficiency of P in *a*-Si:H. This is in stark contrast to the situation for B. Further, we obtain average energies for P incorporation in threefold sites, fourfold sites with four Si neighbors, and fourfold-coordinated sites with one H neighbor and three Si neighbors. However, our results

on P-H complexes are not so traditional. We have found no cases where the typical H-passivated P complexes are even metastable, as they are in *c*-Si. Thus not only do P and B act very differently in *a*-Si:H, but they also both act quite differently than they do in crystalline Si.

In the rest of this section, we shall review the relevant experimental facts. In Sec. II, we shall discuss the methodology and the results will be presented, and then discussed in Sec. III. There is a short conclusion in Sec. IV.

The B nucleus has a quadrupole moment which couples to electric-field gradients and thus appropriate NMR experiments yield information about the symmetry of the B atoms. Since the P nucleus has a spin- $\frac{1}{2}$ and thus no quadrupole moment, the electrical environment cannot be directly probed by NMR nor by any other method that we are aware of. However, extended x-ray-absorption fine-structure (EXAFS) spectroscopy has been used to study the dopant As in As-doped *a*-Si:H.⁵ This work supports the idea that inactive dopants are threefold coordinated, and that active dopants are fourfold coordinated. Presumably the chemistry of P is quite similar to that of As. However, H atoms can cause substantial uncertainty in these conclusions about the local environment, since EXAFS is not sensitive to the H atoms. Reimer and co-workers⁶ reported 20% of the P to be fourfold coordinated, and to exhibit a rapid echo decay due to close association to H clusters. However, later studies by Boyce and Ready^{7,8} did not confirm this, and, in fact, showed no evidence of different configurations of P.

Further, Boyce and Ready studied the spatial near-neighbor correlations of both P and B with H using NMR methods. For B they found that about half of the B had a H neighbor about 1.6 Å away, with some sample-to-sample variations. The results for P were quite different in that the first peak of H neighbors to P was about 2.6 Å. As the investigators noted, this could be attributed to the familiar back bonding of a H to a Si nearest neighbor to a P, as has been proposed for *n*-type crystalline Si. However, the distance of 2.6 Å would require a much smaller angle than calculations give. It is possible that the distance just corresponds to having a nearby Si with a H neighbor. Finally, the

investigators noted that the P tended to be in clusters that contained less than a random amount of H.

We conclude this section with a brief discussion of simple models of P incorporated into a -Si:H. One simple possibility is that P essentially follows the rules of effective-mass theory, as it does in c -Si. That is, the bonding of P is quite similar to the bonding of Si (within a Si network) except that there is one more positive charge and one more electron. This simple model even holds true for H-passivated P in c -Si. The other simple model is that P acts like a classic valence 3 atom, and will thus be incorporated with threefold coordination and will be nondoping in this configuration. Of course, there is no *a priori* guarantee that either of these simple models will prevail, nor that each could be valid in a subset of possible situations.

II. METHODOLOGY

As in our earlier work on B, we used the methods of Demkov *et al.*,⁹ FIREBALL96, who generalized the non-self-consistent local basis Harris functional local-density-approximation scheme of Sankey and co-workers^{10,11} to an approximate self-consistent form. In this approach, Demkov *et al.* exploited the original idea of the Harris functional, which allowed input charge densities in the language of density-functional theory. Spherical atom densities are used as Harris input fragments, and the fragment charges are self-consistently determined. They could (in principle) be determined from the Harris stationary principle, applicable to this class of input fragment densities. The method is efficient, combining the advantages of charge transfer with a fixed atom-centered basis (and therefore efficient look-ups for matrix elements). The long-range Coulomb effects are handled in the conventional way.

For most purposes, the code is quite accurate; the exception being the actual eigenstates in the conduction band. In our calculations, these states are unimportant because they remain unoccupied. A further check of the code was made by comparing the results of the H-passivated P impurity in c -Si with the results of a calculation that is has a larger basis but runs much much slower. Our structural results were identical to these “better” results to within a few hundredths of an Å.¹²

Almost all calculations were performed on supercell samples with about 70 atoms per unit cell using four k points. Again, as a check, a few calculations were performed on supercells of about 230–240 atoms with only minor differences noted. The supercells themselves were very stable and contained either zero or one defect in them. The ones with one defect had one threefold-coordinated atom which was necessary to study threefold-coordinated P. The supercell with no defects had no geometrical or electronic (spectral) defects and the supercell with one defect had one electronically well-localized state on the dangling bond. We note that most theoretical studies are performed on supercells with 15–20 % defects. We believe that such supercells are suspect. The average properties of our supercells, including bond-angle distribution and bond-length distribution, were unchanged in anneals of many picoseconds at temperatures up to 600 K and individual bonds and angles changed only

by small amounts, as would be expected in a glassy substance.¹³

Finally, our modus operandi was to take a stable a -Si:H supercell and replace one Si atom at a time with a P atom. The new supercell was then relaxed to equilibrium. In about one-third of the cases we then annealed the new supercell for a few picoseconds at 600 K. Again, this anneal caused no more than the minor changes in angles and bond lengths that one expects¹³ in an amorphous or glassy substance, and the average properties were unchanged. The change in total energy was typically about a few hundredths of an eV. Admittedly, this is not the way P-doped a -Si:H is fabricated in the lab. However, the original supercells were not constructed in any way resembling lab-fabricated material. In fact, because of time limitations, nobody can construct supercells in a way that is similar to the way the actual material is fabricated. We take the point of view that the test of a supercell sample is its agreement with lab-grown material as far as pair-correlation function, bond-angle distribution, energy density of states (especially a clean gap), a minimal number of defects, and stability upon anneal. Our supercells all pass these tests.

III. RESULTS OF THE CALCULATIONS

A. P not passivated by H

In this subsection we present results of our calculations for P in positions in the a -Si:H network with no H passivation. The configurations investigated were P(4) (a P with four Si neighbors), P(3,1) (a P with three Si neighbors and one H neighbor), and P(3) (a P with only three Si nearest neighbors). In this paper we take the point of view that a H atom passivating a dangling bond is much like another Si neighbor, and we reserve the term “passivated” for a H either between a Si atom and a P atom or on the antibonding side of a Si atom with a P nearest neighbor, although the term is used only for the antibonding configuration with crystalline semiconductors. In the first two cases, P(4) and P(3,1), we started with an a -Si:H supercell with no defects and thus a Fermi level in the gap. The replacement of a Si atom with a P atom moved the Fermi level to the edge of the conduction band. In the case of the supercell with a dangling bond, the Fermi level is pinned at the dangling-bond energy with no P replacement. Since we are only investigating n -type material, we must compare to a starting configuration where the threefold atoms (dangling bond) do not correspond to an occupied state. This can be accomplished by either adding another P atom far away from the dangling bond, or artificially shifting an energy eigenvalue. We found very little difference between the two methods. The results of the energy calculations are displayed in Table I. All energies refer to the energy of the configuration with one Si replaced by one P and then relaxed. The results are further normalized by subtracting the replacement energy in c -Si. Thus a positive energy means that the binding energy is less than in the crystal. However, it is the comparison between different cases in a -Si:H that is important and not the relationship to the crystal. For P(4) and P(3,1), the averages are over eight cases which were chosen at random, while, for P(3), only three cases were available with supercells that we deemed as sufficiently realistic and stable. Since we have never created a good supercell sample where a Si atom contains both a

TABLE I. Average energies for single P configuration in an a -Si:H network. P(4) denotes a P with four Si neighbors, P(3,1) denotes a P with three Si neighbors and one H neighbor, and P(3) denotes a P with three Si neighbors. All energies are with respect to a P atom substituting for a Si atom in c -Si. All entries are energies in eV.

	P(4)	P(3,1)	P(3)
Average energy	-0.64	-0.17	-1.25
Maximum energy	-0.46	-0.02	-1.00
Minimum energy	-0.81	-0.54	-1.39

dangling bond and a H neighbor, we could not investigate a P atom with two Si neighbors and one H neighbor.

From Table I we see the P(3), the threefold-coordinated configuration for P, is overwhelmingly favored energetically (on the average), more than 0.6 eV lower than either of the fourfold-coordinated cases. Among the configurations of fourfold-coordinated P atoms, the one without a H neighbor is almost 0.5 eV more favorable than the one with one H nearest neighbor. This is exactly the opposite of the case for B, where the threefold-coordinated configuration was the least energetically favorable and a B atom favored one H neighbor and three Si neighbors over four Si neighbors. However the magnitude of the energy differences are 2–3 times as large as in the B case. We have not considered the effects of kinetics, but it is very difficult to believe the kinetic effects could overcome these rather large energies. These results are entirely consistent with the NMR measurements of Boyce and Ready, even to the extent of P shunning an H nearest neighbor.

Electronically, the results are as expected. Both the P(4) and P(3,1) configurations dope the material. That is, they produce a shallow donor at the conduction-band edge and increase the number of electrons by one from the Si analog. In our simulations we obtain an extra state at the conduction-band edge that is not localized. Thus the Fermi level is moved up by one half of a state for each P. As might be expected, the fourfold-coordinated P atoms bond much like the fourfold-coordinated Si atoms, just as they do in c -Si, where they dope the material. Further, the threefold coordinated P atoms P(3) act as valence 3 atoms in that they are electrically inert (nondoping) and they do not introduce a midgap-localized dangling-bond state as was the case with threefold-coordinated B. Three-fold coordinated B atoms acted qualitatively like the host Si atoms in the a -Si network, and not as valence 3 atoms.

B. P passivated by H

From the above results we conclude that the low doping efficiency of P in a -Si:H is due to almost all of the P atoms being threefold coordinated. However, for completeness, and to complete the analogies with B in a -Si:H and with crystalline results, we have also investigated the passivation of P with H atoms. B in crystalline Si is passivated with a hydrogen atom placed between the B atom and a neighboring Si atom. We found that this also passivated B in a -Si:H, al-

though the H atom could also be between two Si atoms, one of which is a neighbor to the B atom in question.

The situation for P is not so clear cut. Calculations show that P in crystalline Si is passivated by having a H atom as a fifth neighbor to a Si atom which neighbors the P atom in question. It is also passivated by placing a H atom between the P atom and a neighboring Si atom, but this configuration has a higher energy than the former. However, neither configuration is very stable. In the dark the former configuration dissociates around 100 °C, but is apparently reactivated with illumination.¹⁴ The subject is somewhat controversial,^{3,4} and we shall only discuss the situation in a -Si:H. We have placed H atoms between a P atom and a Si atom in well-annealed stable a -Si:H supercells as well as one H atom between two Si atoms, one of which neighbors a P atom. The supercell samples were then quenched. Although this was tried in many different cases, the complex was unstable in every case. After relaxation (with or without annealing) the configuration shifted into one in which the P had three Si (and no H) neighbors, and all nearby Si atoms had four neighbors which might include Si, P, and/or H atoms. These configuration did, of course, completely passivate the P. The former configuration with a -Si having a fifth H neighbor next to the P is quite similar to the crystalline case. However, the second configuration with a H between the P and Si dissociates in a -Si but is metastable in crystalline Si. Thus P in a -Si:H very much “prefers” to be threefold coordinated and shuns H atoms.

In order to understand better the difference between the {B,H} pair and the {P,H} pair, we note the following: In the case of the {B,H} pair the H can bind to Si near a bond-centered site. Thus the Si bonding to the {B-H} pair is sp^3 , and thus forms a strong bond. This relieves some strain, since B forms short bonds with Si in the crystal. Of course in a -Si:H, the strains can also be relieved by slight readjustments on many Si atoms.

In the case of the {P,H} pair, the H (in crystalline Si) cannot bond to Si near a bond-centered site, because the P’s lone pair fills the space between P and Si. H can only bond at an antibonding site, and this is a weak bond which does not contribute much to strain relief since the Pi-Si bond length is similar to the Si-Si bond length. However, in a -Si:H, there are numerous, more favorable, configurations, as our calculations show.

IV. CONCLUSION

Our calculations support the traditional view that the low doping efficiency of P in a -Si:H is due to the fact that almost all of the P is threefold coordinated, and that threefold-coordinated P in a -Si:H is an inert (nondoping) configuration. Further, threefold-coordinated P is energetically favored (on the average) over fourfold-coordinated P, but of course the distributions can overlap to allow a small amount of fourfold-coordinated P. Further, it is energetically unfavorable for P to have a H neighbor. All of the above are supported by experimental facts. The above situation is almost the exact opposite to the case for B, where we have showed that threefold-coordinated B is energetically unfavorable and that when it does exist, should form a dangling-bond localized state. Further, it is energetically favorable for

B to have a H neighbor (as is born out by experiments). Thus, in short, P in a -Si:H acts according to effective-mass theory which views P as a valence 3 atom, and B as acting like Si with one less nuclear charge and one less electron. This asymmetry is not observed in crystalline Si. However, in a -Si, the possibilities of lowering the energy by substantial relaxation is present to a degree nowhere near possible in

crystalline Si. Further, in a -Si:H, P will not complex with H to form a passivated complex in the same way that it does in crystalline Si.

ACKNOWLEDGMENTS

I wish to acknowledge a number of useful conversations with Professor Dave Drabold of Ohio University.

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