Theory of boron doping in a-Si:H

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For a long time the rather low doping efficiency of B in a-Si:H has been explained by the argument that almost all of the B is incorporated into threefold coordinated sites and that B is inert or nondoping in this configuration. Using *ab initio* molecular dynamics, we have studied the energetics and electronic structure (doping) consequences of B incorporation into a-Si:H both with and without H passivation. Our results suggest that the conventional view is in error and that the low doping efficiency is primarily due to H passivation. These results are consistent with the low doping efficiency of B as well as NMR studies on the large electric-field gradients experienced by the B atoms and on NMR double-resonance studies of B-H neighboring distances. [S0163-1829(97)03428-0]

I. INTRODUCTION

It is well known that the doping efficiency of B in a-Si:H is quite low.[1] The doping efficiency is about 10% at low concentrations of B and falls off to a fraction of a percent as the concentration of B rises. Further, effective doping efficiencies are considerably less because of the filling of band tail and defect states. This low doping efficiency is nearly universally attributed to the belief that almost all of the B is incorporated into threefold coordinated sites and that B is inert or nondoping in this configuration. This is in marked contrast to the situation for c-Si, where the doping efficiency of B is virtually 100%. In crystals all the B atoms substitute for Si atoms and are well described by effective-mass theory. That is, B bonds to the neighboring Si atoms much like any Si atom except that it has one less nuclear charge and one less electron. Thus a shallow acceptor state is created near the valence-band edge and there is one fewer electron to fill the electronic states. Thus, at least at low or moderate temperatures, the Fermi level moves down toward the valence-band edge as more B is incorporated.

We have performed extensive molecular-dynamics (MD) calculations on the incorporation of B into a-Si:H networks and have studied both the energetics and electronic (doping) consequences of B incorporated into the network both with and without H passivation. Our studies strongly suggest that the conventional view is in error and that the low doping efficiency is primarily due to H passivation. Our results are consistent with the low doping efficiency of B, NMR line-shape studies on the B nucleus, and NMR studies of the distance between B-H neighbors. We believe that this work is the first in the *ab initio* investigation of doping in a-Si and one of the first concerning any amorphous material. In a number of ways, it is parallel to our investigation of N doping in tetrahedral amorphous C.[2]

In the rest of this section, we shall review the relevant experimental facts. For low concentrations the doping efficiency of B is about 10% and it drops off as the concentration of B increases. The effective doping efficiency can be much less because of defect states and band tailing, but we shall not be concerned with these problems.

NMR has contributed quite a lot of information about the B environment in a-Si:H. First of all, NMR measurements on the line shape of the B nuclear spins shows that most of the B nuclei contribute to a very broad line.[3,4] Since B has a substantial quadrupole moment, this broadening is due to sizable electric-field gradients and these inhomogeneous electrical effects dwarf the dipolar interaction of the B nuclei with nearby nuclei. The experiments thus show that almost all of the B atoms are not in sites of perfect or nearly perfect tetrahedral symmetry. Although threefold coordinated B is a possible explanation for this effect, it is not a unique explanation. A number of other explanations are possible, including the existence of a nearby H atom breaking the tetrahedral symmetry.

The other piece of NMR evidence is the work by Boyce and Ready[5,6] on the dopant microstructure on B in a-Si:H. Using nuclear double-resonance techniques, these investigators showed that about one-half of all B atoms had a neighboring H atom about 1.4 Å away. The exact fraction was sample dependent. This has very interesting implications. One possibility is that about one-half of all B atoms have dangling bonds that are passivated by a H atom. This implies that B has a much much higher affinity for H than Si does. Further, it makes the assumption that almost all B is threefold coordinated somewhat awkward. If that is the case, then one-half of the B has one H and only two Si neighbors that connect it to the rest of the network. With heavy doping, the structure would be more like silica glass than Si. On the other hand, as noted by the authors, it could indicate that the B dopant tends to be passivated by H as it is in c-Si. In this material, H passivated B dopants by placing itself between a B atom and a neighboring Si atom. In a crude effective mass sense, the B plus a H equals a Si and so the complex is inert or nondoping. Actually, the situation is considerably more complex than this but the complex is nondoping. The energetics of these possibilities will be taken up in this paper.

We conclude this section with a brief discussion of simple

models of B incorporated into a-Si:H. One simple possibility is that B essentially follows the rules of effective-mass theory, as it does in c-Si. That is, the bonding of B is quite similar to the bonding of Si (within a Si network) except that there is one less positive change and one less electron. This simple model even holds true for H passivated B in c-Si. The other simple model is that B acts like a classic valence-three 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

We use the methods of Demkov, Sankey, Ortega, and Grumbach,[7] who generalized the non-self-consistent local basis Harris functional local-density approximation scheme of Sankey and co-workers[8,9] to an approximate self-consistent form. In this approach, Demkov and co-workers 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. As a check, a few calculations were re-run with a self-consistent plane-wave code. The difference between the two methods was minor in all cases tested. A further check of the code was made by comparing the results of the H passivated B impurity in c-Si with the results of a calculation that it has a larger basis but runs much much slower. Our structural results were identical to these ''better'' results to within a few hundredths on an angstrom.[10]

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 B. 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 annealings 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.[11]

Finally, our *modus operandi* was to take a stable a-Si:H supercell and replace one Si atom at a time with a B atom. The new supercell was then relaxed to equilibrium. In about a third of the cases we then annealed the new supercell for a few picoseconds at 600 K. Again, this annealing caused no more than the minor changes in angles and bond lengths that one expects[11] in an amorphous or glassy substance and the average properties were unchanged. The change in total energy was typically about a few hundredth of an eV. Admittedly, this is not the way B-doped a-Si:H is fabricated in the laboratory. However, the original supercells were not constructed in any way resembling laboratory 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 laboratory 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 annealing. Our supercells all pass these tests.

We made several attempts at forming a-Si supercells with a small number of B atoms from a liquidlike starting point. However, all of these attempts failed in that the ensuing supercells had large (15–20 %) numbers of defects, many of which were fivefold coordinated (floating bond) defects and badly strained fourfold coordinated atoms. As with other defect laden supercells constructed by us and others, the gap was essentially obliterated. These cells were rejected as not resembling real a-Si. These difficulties were also present in attempts by us (and others) in making supercells without B inclusions and had nothing to do with B. However, in these flawed supercells we found that B was no more likely to be threefold coordinated than Si was.

III. RESULTS OF THE CALCULATIONS

A. B not passivated by H

In this subsection we present the results of our calculations for B in positions in the a-Si:H network with no H passivation. The configurations investigated were B(4) (a B with four Si neighbors), B(3,1) (a B with three Si and one H neighbors), and B(3) (a B with only three Si nearest neighbors). The B(4) and B(3,1) configurations are very similar in that both have a fourfold coordinated boron atom. However, for B(3,1) one of these four neighbors is a hydrogen atom. This hydrogen atom is not close to any other atoms and its removal would turn the B(3,1) configuration into the B(3) configuration. 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 atom between a Si atom and a B atom. This is the sense that the term is used with crystalline semiconductors. In the first two cases 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 B atom moved the Fermi level to the edge of the valence band. In the case of the supercell with a dangling bond, the Fermi level is pinned at the dangling-bond energy with no B replacement. Since we are only investigating p-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

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

Energy	B(4)	B(3,1)	B(3)
average energy	0.42	0.22	0.65
variance	0.24	0.20	0.20
maximum energy	0.80	0.47	0.90
minimum energy	0.02	−0.11	0.42

adding another B 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 B 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. For B(4) and B(3,1), the averages are over ten cases that were chosen at random, while for B(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 dangling bond and a H neighbor, we could not investigate a B atom with two Si and one H neighbors. We note that our calculations explain the observed fact that a substantial fraction of B atoms have a H nearest neighbor.

From Table I we see that the B(3,1) is the most favorable configuration energetically. Next, about 0.2 eV higher on the average, the B(4) configuration occurs. However, the distributions for these two configurations do overlap. Finally, more than 0.4 eV above B(3,1), the B(3) configuration occurs. Without some rather unusual effects from the kinetics (which we have not considered), it is difficult to believe that much threefold coordinated B should exist in a-Si:H. Further, it appears that H atoms significantly favor B atoms with three Si neighbors over Si atoms with three Si neighbors. All three cases can be considered to employ sp^3 bonding.

Electronically, the results are equally interesting. As expected, both the B(4) and B(3,1) configurations dope the material. That is, they produce a shallow acceptor at the valence-band edge and decrease the number of electrons by one from the Si analogue. That is, in our simulations we obtain an extra state at the valence-band edge that is not localized. Thus the Fermi level is moved down by one-half of a state for each B. As might be expected, the fourfold coordinated B atoms bond much like the fourfold coordinated Si atoms just as they do in c-Si where they dope the material. However, we also find that the the B(3) configuration bonds much like the analogous threefold coordinated Si atom. Structurally, we find that the B(3) configuration is very similar to the configuration with the Si dangling bond if the dangling bond is totally unoccupied. That is, the bond angles for the threefold Si and the threefold B differ by only two degrees on the average. This is to be compared to angular changes of order ten degrees when the occupation of the Si

dangling bond is changed (using the same self-consistent code). Further we find a localized dangling-bond energy eigenvalue whether a Si or a B atom occupies the threefold coordinated site. Since this is an important point, the result was checked using a self-consistent plane-wave code with a much larger basis. The localization of the dangling-bond state decreased with the greater basis for both the Si case and the B case, but they were both recognizable as localized states. We should mention that all methods are somewhat unreliable in calculating the properties of unoccupied states. This problem is aggravated by a limited basis.

The B(3) configuration is not a doping configuration, but neither is it electrically inert. A threefold coordinated Si atom (dangling bond) contributes a localized state in the gap that can accommodate zero, one, or two electrons. The configuration contributes one electron and thus dangling bonds tend to pin the Fermi level. With B(3), a localized state is still formed, but it contributes no electrons. Thus, assuming the material is already p-like, it does not effect the Fermi level. However, the localized dangling-bond state is still there.

B. B passivated by H

From the above results we conclude that the low doping efficiency of B in a-Si:H is probably not due to threefold coordinated B. The configuration has a high formation energy and also calculations show that it produces a localized state in the gap that is not observed. Thus we turn to H passivation for the explanation. This avenue has already been suggested by Boyce and Ready.

As is well known, H passivation of B in c-Si occurs when a H atom is lodged between a B atom and one of its Si nearest neighbors. Our self-consistent code gives results for the structure of this configuration that are in excellent agreement with other methods.

We have investigated the passivation of B in a-Si:H in a similar way. That is, first we placed a H atom halfway between a B atom and a neighboring Si atom and then relaxed the structure. About 1/3 of the time we then annealed the supercell as described earlier, but this never caused an appreciable change. Structurally our results were similar to the case in c-Si except the B-H-Si bond angle never remained close to 180°. It varied between 130° and 160° and the B-H distance was about 0.3 Å less than the Si-H distance. The B-H combination is often called a B-H pair. Thus the B-H-Si configuration, like its crystalline analogue, has the H placed between a B atom and a neighboring Si atom, but with a distribution of bond angles. The B-H pair in c-Si is known to be unstable[12] at a temperatures above 150 °C and the same may be true in a-Si. We have not investigated this point. Further, in c-Si there is an infrared mode associated with a reasonably well localized mode at about 1850 cm^{-1} involving the Si-H-B bond.[13] However, because of the large distribution of angles and surroundings, this mode would be hundreds of cm^{-1} wide in a-Si. The energetics of the situation are given in Table II where the configuration is referred to as B-H-Si, again with the zero of energy set by the crystalline case. In order to check for further possibilities we also inserted H between two Si atoms, one of which was a nearest neighbor to a B atom. This configuration, called the B-Si-

TABLE II. Average energies for B-H-Si and B-Si-H-Si complexes in an *a*-Si:H network. Details of the configurations are given in the text. All energies are with respect to the B-H-Si complex in *c*-Si and all energies are in eV.

Energy	B-H-Si	B-Si-H-Si
average energy	16.27	16.30
variance	0.18	0.24

H-Si configuration, consists of a bond centered H between two Si atoms where one of the two Si atoms has the B atom as a neighbor. Interestingly enough, this configuration had virtually the same energy distribution as the first case. Further, both cases led to a passivation of the B atom into an inert or nondoping configuration. Finally, we tried to introduce H atoms as a fifth neighbor to the B atom or nearby Si atom. In all of these trials, the H always moved to a position between a B-Si or Si-Si pair. We believe that both of these configurations in Table II would lead to significant electric-field gradients at the B site, although only one of them had H neighboring the B atom.

It is impossible to say with certainty that a significant amount of H will be incorporated as described above. That is, the energetics of H incorporation into doped or undoped *a*-Si:H is sufficiently murky to do this. We refer to the fact that as *a*-Si:H samples are fabricated in the laboratory with more and more H, the number of dangling bonds does not decrease. We have seen no convincing explanation for this. However, since the H passivation of B dopants does occur in *c*-Si, it is very difficult to believe that it does not also occur in *a*-Si:H with its great number of H atoms.

IV. CONCLUSION

Our calculations strongly suggest that the low doping efficiency of B in *a*-Si:H is not due to threefold coordinated B in that this configuration of B is quite unfavorable energetically and the configuration produces a local state in the gap. Further, our calculations show that the low doping efficiency could easily be due to H passivated B and this explanation is in agreement with known experimental facts. That is, the experiments of Boyce and Ready can be explained by assuming that approximately one-half of the B atoms are passivated with a B-H-Si bond and the remaining B are passivated by a B-Si-H-Si bond. This explanation is also consistent with the NMR line-shape studies and the low doping efficiency of B.

ACKNOWLEDGMENTS

[1] See, for example, K. Winer, R. A. Street, N. M. Johnson, and J. Walker, Phys. Rev. B **42**, 3120 (1990).

[2] P. Stumm, D. A. Drabold, and P. A. Fedders, J. Appl. Phys. **81**, 1289 (1997).

[3] S. G. Greenbaum, W. E. Carlos, and P. C. Taylor, Solid State Commun. **43**, 663 (1982).

[4] S. G. Greenbaum, W. E. Carlos, and P. C. Taylor, J. Appl. Phys. **56**, 1874 (1984).

[5] J. B. Boyce and S. E. Ready, Phys. Rev. B **38**, 11 008 (1988).

[6] J. B. Boyce and S. E. Ready, J. Non-Cryst. Solids **97&98**, 345 (1987).

[7] A. A. Demkov, J. Ortega, O. F. Sankey, and M. P. Grumbach, Phys. Rev. B **52**, 1618 (1995).

[8] O. F. Sankey and D. J. Niklewsk, Phys. Rev. B **40**, 3979 (1989).

[9] O. F. Sankey, D. A. Drabold, and G. B. Adams, Bull. Am. Phys. Soc. **36**, 924 (1991).

[10] Yu Zhou, Rolf Luchsinger, and Peter F. Meier, Phys. Rev. B **51**, 4166 (1995).

[11] P. A. Fedders and D. A. Drabold, Phys. Rev. B **53**, 3841 (1996).

[12] M. Stavola, S. J. Pearton, J. Lopata, and W. C. Dautremont-Smith, Appl. Phys. Lett. **50**, 1086 (1987); T. Zundel and J. Weber, Phys. Rev. B **39**, 13 549 (1989).

[13] G. D. Watkins, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 147.