Doping and the Fermi Energy in Amorphous Silicon

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The doping of hydrogenated amorphous silicon is discussed within the context of Mott's $8-N$ rule, and found to have properties distinctly different from dopants in crystalline silicon. A unifying description of dopant and defect states based on the position of the Fermi energy is given. Some possible consequences of the $8-N$ rule for the deposition and structure of *a*-Si:H are also discussed.

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In 1967 Mott introduced the "$8-N$" rule to account for the absence of doping in covalent amorphous semiconductors.[1] The suggestion was that each element in the material has all its electrons in bonds and so takes on its natural coordination determined by the number of valence electrons N. Thus the coordination of Si is 4, of P is 3, and of Se is 2, etc. (Note, however, that elements in groups I–III are expected to have coordination N.) This rule expresses the complete absence of topological constraints in a random covalent network so that the lowest energy state is determined only by the local chemistry. The most important apparent consequence is that substitutional doping cannot occur in an amorphous semiconductor because this process relies on one atom having an electron (or hole) not in a bond. It therefore came as some surprise when doping was demonstrated in hydrogenated amorphous silicon (a-Si:H).[2] This material can be made both *p* type and *n* type by the addition of boron, phosphorus, or other elements, and the Fermi energy can be moved over a large fraction of the band gap. The interpretation of these properties in terms of substitutional doping has never been seriously doubted.

In unhydrogenated *a*-Si, the Fermi energy cannot be moved by doping because there is a very large density of defects. From their ESR properties these defects are identified as silicon dangling bonds (three-fold coordinated silicon), and as such their existence also violates the $8-N$ rule.[3] In the face of this experimental evidence, it seems necessary to abandon the $8-N$ rule, at least for amorphous silicon. However, since the rule expresses the absence of topological constraints, its violation implies that such constraints must be present. In fact, Phillips has argued that the ideal glass has an average coordination of 2.4, and so silicon is indeed constrained by its higher coordination.[4]

The topological constraints of overcoordination can be relieved by lowering the average network coordination number. Since this can be achieved by including dangling bonds or bonded hydrogen in the network, it is easy to understand why dangling bonds do not obey the $8-N$ rule and why a very low density of defect states is possible in *a*-Si:H. However, if the topological constraints act so as to *reduce* the coordination of the silicon network, it seems hardly possible that a dopant atom such as phosphorus or boron should be constrained by the same topology to *increase* its coordination from 3 to 4. From this point of view, then, substitutional doping is very difficult to understand. Adler makes a similar point in his discussion of defects in *a*-Si, and suggests that the problem is resolved by the formation of dopant-defect pairs in which the dopant is fourfold coordinated while the total defect energy is low enough to be realistic.[5]

This paper describes an alternative way of understanding doping which leads to some verifiable predictions, and which, if correct, gives insight into some general properties of amorphous semiconductors. The model is based on two main propositions. The first is that substitutional doping falls within a modified form of the $8-N$ rule, and in fact only occurs under conditions when the rule is obeyed. The modification is to include the possibility of charged states at the time of deposition, and to apply the $8-N$ rule to the charged atom. Thus, although neutral phosphorus (P^0) has five valence electrons and so should have coordination 3 (P_3^0), a positive phosphorus atom has only four electrons, and by the $8-N$ rule should have coordination 4 (P_4^+). This state, of course, represents a substitutional donor under conditions when the Fermi energy E_F is below the donor band. In this way, the presence of a dopant atom is consistent with the requirement of a low-energy bonding configuration. The second proposition is that the position of E_F plays the crucial role in determining the number of electrons available to the impurity atom. Thus, E_F is not allowed to move up to the donor level during deposition because the occupied donor states (P_4^0) are in violation of the $8-N$ rule. Instead, the relative concentrations of P_4 and P_3 states will always adjust themselves to maintain an empty donor level. A schematic density-of-states diagram illustrating the different configurations is shown in Fig. 1, and similar arguments apply to p-type doping.

This model implies that the doping process is characteristically different in an amorphous semiconductor compared with a crystal. Doping in a crystal occurs through the topological constraint of the periodic lattice. A neutral donor level is readily obtained, and the doping process is generally independent of other impurity or defect states present. In contrast, doping in an amorphous semiconductor can only occur in the presence of the localized gap states that maintain ionized donor levels. The doping is self-limiting in the sense that the doping efficiency (the fraction of impurity atoms in fourfold coordination) must drop as E_F approaches the band edges.

There is some experimental evidence which supports this model, although clearly more definitive data is needed. dc conductivity measurements find that E_F never approaches closer than 0.2–0.3 eV from the mobility edge[2] whilst ESR data find no evidence of occupied donor or acceptor levels.[6] A reasonable measure of the fraction of phosphorus in fourfold coordination can be made by equating their number to the density of compensating charged defects as measured by luminescence, ESR, and photothermal deflection spectroscopy.[7,8] These results in Fig. 2 show that the doping efficiency, η, drops steadily with increasing phosphorus or boron content. Since most of the shift of E_F has occurred at a doping level of 10^{-4}, it is evident that η drops very rapidly with further shifts of E_F.

The presence of only P_4^+ states in doped a-Si:H implies that compensating defects must also be present. To this extent our model is an extension of that proposed by Adler.[5] However, in the present model, the nature of those defects is not important to the dopant atom. Instead, its properties are determined only by the position of E_F, and as I show below, this leads to several interesting predictions. The central role of E_F also allows us to make a connection to the properties of defects in doped a-Si:H. It is observed that the density of dangling bonds increases with doping but decreases again with compensation.[7,8] The mechanism was argued to be an autocompensation process, in which the defect energy decreases as E_F moves away from midgap and the occupancy of the defect changes. This observation can also be understood in terms of the $8-N$

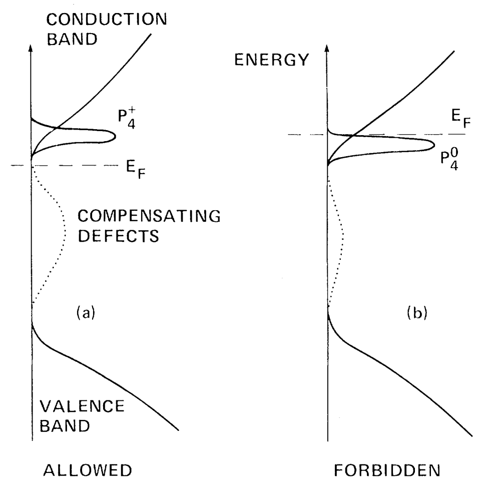

FIG. 1. Schematic density-of-states diagram showing (a) fourfold coordinated phosphorus allowed by the $8-N$ rule, where the Fermi energy E_F is below the donor level (P_4^+); and (b) forbidden fourfold configuration with occupied donor levels (P_4^0).

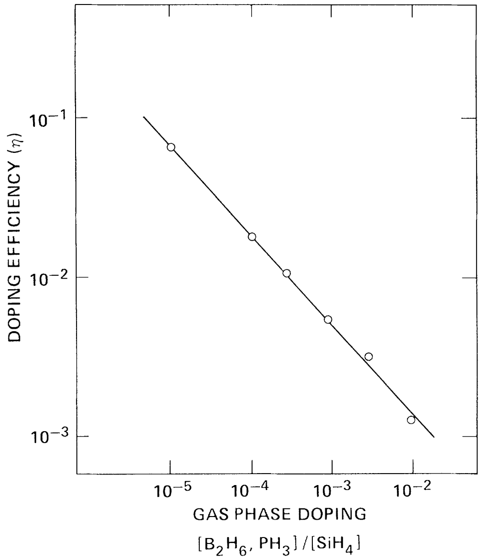

FIG. 2. The doping efficiency η of a-Si:H for different doping levels. The results are obtained from the data in Refs. 7 and 8.

rule, since a doubly occupied Si dangling bond has five electrons. Therefore, although the neutral dangling bond does not obey the $8-N$ rule and is introduced solely by topological necessity, charged dangling bonds do obey the rule and so are favored energetically.

Thus the densities of both dopants and defects are controlled by the position of E_F and so fall within a single unifying concept. In fact, a simple description of the balance between the two types of gap states can be given, as follows. The model proposes an equilibrium between threefold and fourfold coordinated atoms, with the dopant (fourfold) concentration, n, balanced by an equal density of compensating defects, D. The reaction in n-type material is therefore

$$P_3{}^0 \rightleftharpoons P_4{}^+ + D^- .$$

From the law of mass action, we have

$$(N_0 - n)/n^2 = \text{const},$$

where N_0 is the total phosphorus concentration. When the doping efficiency η is low ($n \ll N_0$),

$$\eta = n/N_0 \simeq \text{const}/N_0{}^{1/2}.$$

The predicted dependence on $N_0{}^{1/2}$ agrees with the data in Fig. 2. A similar square-root dependence of η, again for both boron and phosphorus, has also recently been observed in a-Ge:H.[9]

In the remainder of this paper I discuss some speculative consequences of the idea that the dopant and defect structure is determined only by the position of E_F and the $8-N$ rule. For example, suppose that during deposition, the phosphorus doping is sufficient to move E_F into the conduction-band tail. A silicon atom forming a band-tail state below E_F will contain five electrons which is in violation of the $8-N$ rule, and therefore, not a stable state. Instead, such a state should form a negative dangling bond ($Si_3{}^-$). Consequently, E_F can never move into the band tails; either the doping efficiency will drop, or else the band tail itself will change shape, possibly becoming sharper as states are taken away from below E_F to become defects. The prediction is that in doped a-Si:H, E_F can never lie in a large density of states. Instead, E_F forms a demarcation energy separating states of qualitatively different bonding character. In effect, the structure will adjust until a gap opens at E_F. (Note that this result only applies to states obeying the $8-N$ rule. E_F can lie in large density of states which are introduced by topological constraints, such as dangling bonds in unhydrogenated a-Si.) The experimental evidence for this proposal is rather unclear. Our data[7,10] indeed find a low density ($\leq 10^{17}$ cm^{-3}) of occupied band-tail states in doped a-Si:H. However, other measurements[6] report values as high as 10^{19} cm^{-3}.

So far the effects have been considered in terms of the bulk equilibrium Fermi energy. However, the bonding configurations are determined during deposition so that the relevant parameter is the surface Fermi energy. For example, if the surface is positively charged during deposition, the fraction of fourfold coordinated phosphorus should be enhanced because E_F is held down. Similarly, boron doping would be enhanced at a negative surface. By using this effect, it might be possible to improve the doping properties of a-Si:H, provided that there was no structural relaxation in the bulk to reverse the process. Although the surface bias will usually be negative in the glow discharge process, some control is possible, and so this prediction should be open to experimental test.

Another consequence concerns the influence of electronic excitation for which the relevant parameter is the quasi Fermi energy. Consider the deposition of undoped a-Si:H in the presence of strong illumination. If the quasi Fermi energy moved into the band tails, then the $8-N$ rule would predict an increase in the dangling bond density just as discussed earlier for doped a-Si:H. Again this prediction can be tested experimentally.

Finally, there are effects that can occur after deposition. One example is the structural change caused by strong illumination,[11] which some experimental evidence associates with the creation of dangling bond defects. Following the previous discussion, an electron excited to a conduction-band-tail state is, in principle, unstable and should result in the formation of a negative dangling bond. Usually this change will not occur because the rigid covalent network prevents structural rearrangements in the bulk of the sample. However, if structural relaxation can occur, then the dangling bond will result. We cannot predict when the relaxation will occur, as this presumably depends on particular local configurations which allow structural changes. The present model predicts a direct link between the photoconductivity of a-Si:H and the photostructural change, because photoconductivity is a measure of the density of electrons near the conduction-band edge.

A second example of a structural change is the observation of field-enhanced doping.[12] Again, the change is the response to a shift in the Fermi energy and can be explained on the basis of the $8-N$ rule as before.

From these examples I propose that an incipient photostructural instability is a universal property of any photoconductive amorphous semiconductor simply because the stable structure is a function of the position of E_F. The extent to which the instability is realized depends on the details of the relaxation and local reconstruction, which cannot be addressed here, and which will differ from one material to another.

In summary, I suggest that the position of E_F plays a determining role in the density and structure of localized states in *a*-Si:H. Substitutional doping can occur within the context of the $8-N$ rule but with limitations to the doping process which distinguish the doping of amorphous semiconductors from that of crystals. The present model emphasizes that both the doping efficiency and the defect density vary with the impurity concentration. An extension of these ideas to explain some nonequilibrium phenomena in *a*-Si:H is also suggested.

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Spin-Glass with Local Uniaxial Anisotropy

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A Heisenberg spin-glass with local uniaxial anisotropy is studied within replica mean-field theory, including consideration of replica-symmetry breaking. It is shown that it represents a very rich model with much to offer as a test bed for comparison of theory and experiment. The explanation of recent experiments on *Zn*Mn, *Mg*Mn, and *Cd*Mn is one of its consequences.

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The spin-glass[1] remains one of the more enigmatic unsolved problems of modern solid-state physics, having aspects quite contrary to those of conventional physics; such as an apparent practical breakdown of ergodicity, signaled by dramatic history dependence. However, for isotropic spin-glasses there has emerged a folklore of connections between experimental consequences and theoretical "fingerprints" in replica mean-field theory, a theoretical treatment in which the physical disordered system is mapped into an effective pure one involving replicated spins interacting through more complicated interactions and then analyzed in terms of a sophisticated mean-field theory.

In conventional pure systems with short-ranged interactions mean-field theory is at best approximate and may predict transitions in situations where fluctuations remove these transitions. By contrast, for spin-glasses the replica mean-field predictions are in reasonable qualitative accord with experiment while numerically exact evaluations[2] of Gibbs thermodynamic functions for short-range models in dimensions three or less