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Effect of lattice connectivity on the electronic structure of an amorphous semiconductor

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Within the structure of *a*-Si the addition of hydrogen can be thought to produce a decrease in the connectivity of the lattice, compared with the ideal fourfold-coordinated amorphous lattice. We simulate this effect with a Hamiltonian of the Weaire and Thorpe type, within which a proportion c of adjacent sp^3 orbitals are eliminated. In this model the width of the gap is determined by the upper edge of the bonding p band and the lower edge of the sp antibonding band. We found that, as c increases the sp bands decrease in width while the pure p bands (the deltas in the Weaire and Thorpe model) do not modify their position. This causes an increase in the size of the gap which is in accordance with experimental observations for hydrogenated amorphous silicon. The results suggest that the effective dimension of the space where the carriers are constrained to move plays an important role in amorphous semiconductors.

I. INTRODUCTION

Intrinsic *a*-Si has a concentration of approximately 10^{19} spin/cm^3. These paramagnetic centers correspond to localized states near the Fermi level and can be identified with dangling bonds that is, singly occupied sp^3 orbitals which cannot satisfy the covalent bonding because of steric hindrances. In order to remove these defects from the gap region, it is usual to incorporate hydrogen, which saturates the dangling bonds. However, the concentration of hydrogen in $a\text{-Si}_{1-x}\text{H}_x$ required to obtain a gap useful for technological applications is about two orders of magnitude larger than the concentration of dangling bonds. The natural question is, then,[1] what is all this extra hydrogen doing?

Our hypothesis is that the extra hydrogen breaks some Si–Si bonds and creates an additional number of Si–H bonds. This process should relax the lattice strains. That is because the mean number $\langle Z\rangle$ of Si nearest neighbors of each silicon atom decreases toward the ideal value $\langle Z\rangle \leq \sqrt{6}$ predicted by Phillips[2] for the unconstrained network in three dimensions. Simultaneously, the electronic properties will be determined by the topology of the remaining Si–Si lattice. This has a lower connectivity and hence causes an increase of the gap.

There are very important papers[3–5] in the literature which discuss the nature of the isolated Si–H bonds by considering a single defect in a Bethe lattice[4] or a diamond crystal.[3,5] In general they are consistent with the idea that hydrogen is responsible for an expansion in the band gap of local density of states with a larger effect on the valence band. However, this work cannot account for the effects of the change in the connectivity of the lattice and this justifies the present model.

II. THE MODEL

We consider 64 Si atoms placed on a diamond lattice represented by the tight-binding Hamiltonian,

$$\hat{H}=\sum_i \sum_{\substack{\mu,\mu'=1\\ \mu\neq\mu'}}^{Z_i} V_1 |i\mu\rangle\langle i\mu'| + \sum_i \sum_{\mu}^{Z_i} V_2 |i\mu\rangle\langle i_\mu \mu| \ , \tag{1}$$

with the Thorpe-Weaire[6] parameters: $V_1=-2.5$ eV and $V_2=-6.75$ eV.

As shown in Fig. 1, index i labels the Si atoms and index μ labels each of its Z_i sp^3 orbitals which are bound to a nearest-neighbor Si atom. The pure case with all $Z_i=4$ is exactly that which was considered by Thorpe and Weaire.[6]

Each cluster surface is connected to the opposite one by periodic boundary conditions. This is equivalent to the molecular unit cell approach[7] calculated at the Γ point $(\mathbf{k}=\mathbf{0})$, and this guarantees that the calculated band edges are exactly the same as those of the infinite crystal. In this case the width B of both the valence and the conduction band (see Fig. 2) is given by

$$B=ZV_1=(d+1)V_1 \ . \tag{2}$$

Here d is the dimensionality of the lattice. This result is valid for the lattice formed by considering only the sp^d hybrids; these are the diamond lattice $(Z=4,\ d=3)$, the honeycomb lattice $(Z=3,\ d=2)$, and the linear chain $(Z=2,\ d=1)$.

In order to simulate a $a\text{-Si}_{1-x}\text{H}_x$ lattice, we randomly remove a proportion $c=x/(4-4x)$ of Si–Si bonds; these are

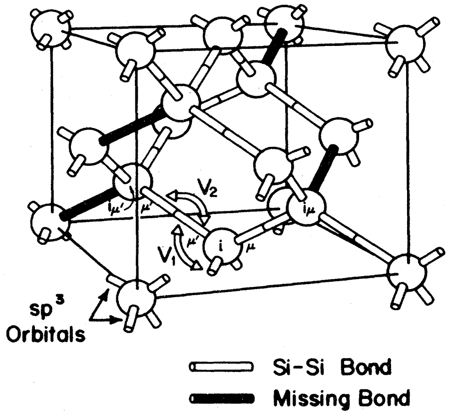

FIG. 1. This figure shows the structure of the amorphous lattice with the parameters of the Hamiltonian.

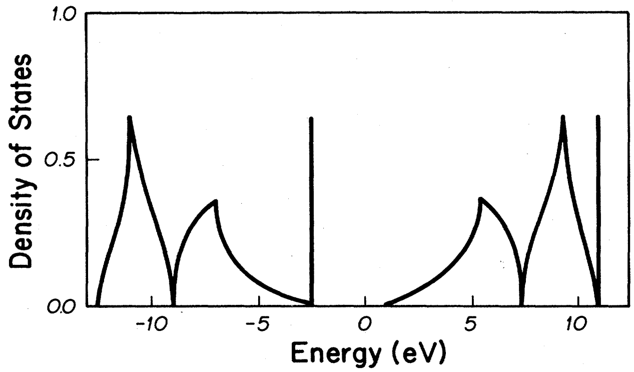

FIG. 2. This figure shows the density of states for the diamond lattice according to the work of Thorpe and Weaire (Ref. 6).

the missing bonds of Fig. 1. Since the wave function coming from states in the band edges do not mix with the Si–H bond states, the whole structure of these sp^3 hydrogen-saturated orbital should be topologically equivalent to considering only the backbone structure.

III. RESULTS

We diagonalized the Hamiltonian (1) and studied the dependence of the band edges on c by averaging the values of the band edges over an ensemble of six clusters. We obtained the following results: (i) The upper edges of the conduction band and valence band (deltas in Fig. 2) do not depend on x, although their weight decreases as x increases. (ii) The lower edges of both bands are pushed toward higher energies as x increases. (iii) The calculations of the inverse participation ratio of the eigenvectors shows that the states at the lower edges of both bands are more localized than those at the center of the bands.

The result (i) is easy to understand. It was already pointed out[7] that the delta functions, and hence the broadened peak which is found in more realistic calculations, are a consequence of the short-range order. In a perfectly coordinated structure with $Z=4$, 3, 2, without dangling bonds, each delta function contains[8] $(z-2)/2$ states per atom. This effect is the origin of the observed decrease of the degeneracy of the delta functions with $\langle Z\rangle$, while their position is fixed at $E=V_1\pm V_2$.

On the other hand, the pure s states at the bottom of the valence and conduction band are a Brillouin-zone effect[7] and hence depend on the long-range order. When $\langle Z\rangle$ is decreased, this situation can only be obtained inside of a large enough island of perfectly coordinated atoms. This domain has a very low probability of occurrence for the size of cluster that we considered. The edge states obtained from our model are representative of the bulk states, and it seems natural that their position depends strongly on $\langle Z\rangle$. This is consistent with the result of (ii).

Recently, it has been shown[9,10] that the quantum eigenfunctions of a disordered system could be characterized by means of a fractal dimension defined in the same spirit of that used[11,12] to measure the connectivity of self-similar lattices in the classical percolation problem. Here we use a fractal dimensionality analogous to that of Ref. 9, in which the fractal dimension d_{eff} of wave functions at the band edges can be evaluated from the bandwidth B as a generalization of Eq. (2), that is,

$$d_{\text{eff}}=B/V_1-1\ . \tag{3}$$

From (i) and (ii) we see that (3) characterizes the fragmentation of wave functions at the lower band edges of each band. Definition (3) might not be quantitatively equivalent to that of Ref. 10. However, their qualitative behavior is the same and (3) is far more simple for our purpose. As the present model is a quantum problem, the fragmentation of eigenfunctions arises not only from the topology of the Si–Si lattice to which the electrons are constrained to move, but also by the additional effect of quantum interference[13,14] which is most significant at the band edges, in accordance with (iii). The codimension $d-d_{\text{eff}}$ is then an index of the extent to which the eigenfunctions in the band edges fail to fill the embedding space. As x increases, $d-d_{\text{eff}}$ also increases.

In Fig. 3 the circles show the fractal dimensionalities for some ordered lattices (diamond, honeycomb, and linear chain). The squares show the fractal dimensionality for the conduction band as a function of $\langle Z\rangle$. The triangles correspond to the valence band. Although the behavior of conduction and valence bands is slightly different, it can be stated that the random fluctuations of Z above the mean value $\langle Z\rangle$ of the disordered system allows ramification to occur. This fact produces a d_{eff} larger than that of a periodic system with the same $\langle Z\rangle$. The slope of d_{eff} vs $\langle Z\rangle$ evaluated for the conduction band (squares in Fig. 3) is greater than that of the valence band (triangles in Fig. 3). This shows that the quantum interference caused by the connectivity disorder is also stronger in the conduction band.

Although our model could be considered an oversimplified one, it contains much fundamental physics, which suggest that the main effect of the disorder of the lattice con-

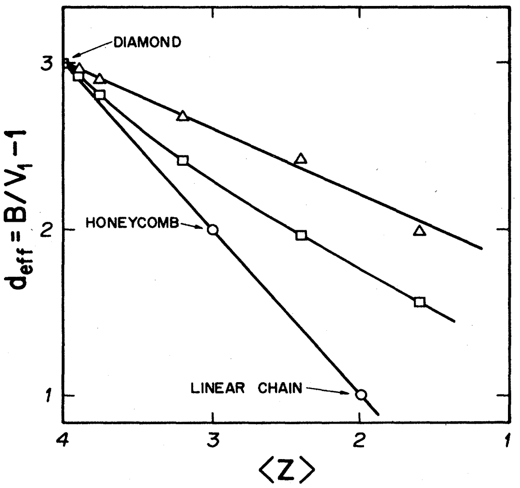

FIG. 3. This figure shows the dependence of the fractal dimension with the mean number of coordination for various crystalline structures (represented by circles) and amorphous structures (represented by triangles for the valence band and squares for the conduction band).

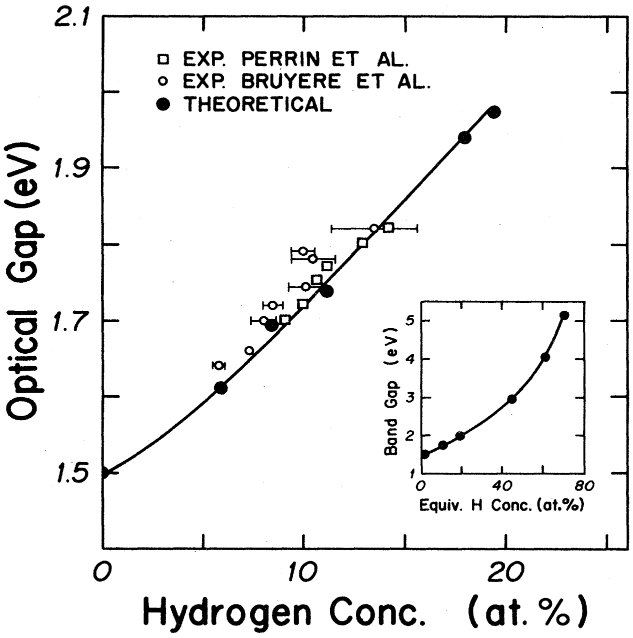

FIG. 4. Here the experimental data (from Refs. 16 and 17) for the evolution of the band gap in $a\text{-Si}_{1-x}H_x$ are compared with the theoretical calculations.

nectivity is to push the conduction band toward higher energies. The top of the valence band comes from states which are linear combinations of p orbitals. Since these have a local character, the center of this band is not affected by the lack of long-range order. Of course, we do not discard the erosion of the top of the valence band with the concentration of H found from ultraviolet photoemission (UPS) experiments.[15] In our model this fact is represented by the loss of the weight of the p band. However, from the point of view of the definition of the band gap, this effect should be smaller than the erosion of the conduction band. Another point to be commented on is that the solution of our model on an infinite cluster would include Lifshitz tails[16] originated in large islands of perfectly coordinated silicon; however, their contribution to the density of states is exponentially small and does not affect the optical gap E_g defined by the bulk of the bands.

In Fig. 4 we compare the experimental dependence of the optical gap with x in $a\text{-Si}_{1-x}H_x$ from Refs. 17 and 18 with that obtained from the present model. Observe that the optical gap at $x=0$, E_0, is the adjusted parameter. In the Weaire and Thorpe model the magnitude of the gap has little meaning because of the infinitesimal width of the P band. In turn, an adjustable E_0 allows the inclusion[19] of effects which do not depend much on the hydrogen concentration, such as the erosion of bands caused by presence of odd rings.

The agreement among the slopes of the theoretical and experimental optical gap gives strong support to the initial hypothesis, and must contain some of the physics which governs the phenomena.

IV. CONCLUSION

The present model shows the importance of the effective dimensionality of the lattice through which the electrons are moving. This allows an interpretation of the effect of nitrogen[20] in $a\text{-Si}_{1-x}N_xH$. Since most of N atoms have only three neighbors, as in Si_3N_4 crystals, the connectivity of the lattice is lowered. d_{eff} and $\langle Z \rangle$ are then lowered as x increases and this translates into an increase of the gap.

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