PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN 49 (1980) SUPPL. A p. 1175–1178

KINDS OF DISORDER AND THE ELECTRONIC STRUCTURES OF TETRAHEDRAL AMORPHOUS SEMICONDUCTORS

Morrel H. Cohen, H. Fritzsche, J. Singh and F. Yonezawa

University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637
USA

Research Institute for Fundamental Physics
Kyoto 606, Japan

In an elemental tetrahedral amorphous semiconductor, such as Si or Ge, there is both quantitative and topological disorder. The topological disorder includes both coordination defects and the ring statistics. The quantitative disorder includes bond-length, bond-angle, and dihedral-angle variation. Using an accurate tight-binding representation for Si, we have shown that the bond-length and bond-angle disorder are relatively unimportant. Neglecting them, assuming coordination defects are suppressed, and including all nearest neighbor interactions, we find that both the valence and conduction band edges are Lifshitz limits, the former sensitive only to the dihedral-angle disorder and the latter only weakly sensitive to the presence of odd rings. Extensions of these results enable one to understand semiquantitatively the differences in density of states between crystalline and amorphous Si as well as predict variations among different amorphous semiconductors.

I. Introduction

With recent rapid improvements in the experimental techniques for making amorphous silicon (a-Si) [1, 2], the need for a deeper theoretical understanding of electronic structures of amorphous semiconductors has become pressing, important not only for further improving the properties of a-Si, but also for theoretical prediction of the possibility of other high quality amorphous semiconducting films. The work presented here is an attempt to provide such understanding. In particular, we wish to ascertain the origin of the tails of localized states near the band edges and how the different kinds of disorder present in the amorphous structure affect these tails.

We represent the amorphous structure by an ideal continuous random network [3, 4] (CRN). We thus exclude coordination defects in view of recent success in suppressing them by the addition of H and F. The disorder in the semiconductor then arises from bond-angle (θ), bond-length (l) and dihedral-angle (ϕ) variation, together with topological disorder.

Using an s-p^3 tight-binding scheme for the energy levels of Si, including all interactions through second-neighbors together with a corresponding deformation potential theory, one finds [5, 6] from the existing structural models for Si that the bond-length disorder is of least importance and expected to produce energy fluctuations of only $\sim$10 meV. The bond-angle disorder is more important and is expected to produce energy fluctuations of $\sim$0.2 eV at the top of the valence band and $\sim$0.15 eV at the bottom of the conduction band. The dihedral-angle disorder and topological disorder are more important and are expected to produce comparable effects. The next sections deal with them, assuming that bond-length and bond-angle variation does not change the matrix elements.

A relatively large dihedral-angle disorder exists due to the relative ease of rotation around a bond. The dihedral-angle distribution is given roughly by

$$P(\phi) = A(2/3 \sin^2 \frac{3\phi}{2} + 1/3) \tag{1}$$

(A is a constant), with peaks at the staggered configuration $\phi = 60°; 180°$. In dealing with dihedral-angle disorder, we limit ourselves to nearest-neighbor interactions. Using an sp^3 bond basis, there are six matrix elements, viz. V_1 through V_6 as shown in Fig. (1). The interactions V_4, V_5, V_6 are dihedral-angle dependent and can have a variation of $\sim$1.0 eV, although the sum $V_4 + V_5 + V_6$ is constant.

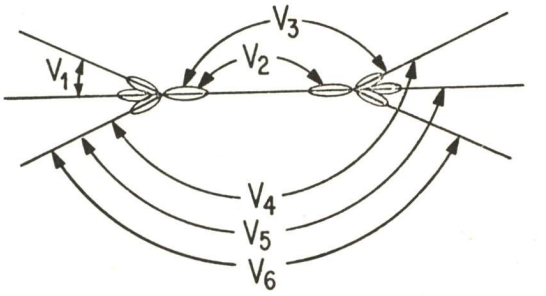

Figure 1 Matrix elements of the Hamiltonian using sp^3 basis and nearest-neighbor interactions

There are four invariants in the problem, viz. V_1, V_2, V_3 $(V_4 + V_5 + V_6)$. An eigenvalue involving only these invariants will be unaffected by dihedral-angle disorder.

We now examine the limits of the spectra arising from our model. This is done by making use of Schwartz inequalities together with the relationships among the matrix elements $V_4(\phi)$, $V_5(\phi)$, $V_6(\phi)$ and their limits. For silicon (we can generalize the results to other tetrahedral semiconductors), we find that the perfect nearest-neighbor order assumed in our model gives rise to well-defined bands. The bottom of the valence band is s bonding and involves the invariants discussed above. This edge is a normal edge, and there exist no localized states near it. The top of the valence band is p-bonding, and the energy is not invariant. The limit is reached by wavefunctions confined to regions which are crystalline-like and have locally the character of the Γ_{25}' states in the crystal. This makes the problem similar to the Lifshitz alloy problem [6, 7]. Localized states are expected at this edge, and the width of the tail of the localized states depends upon the probability distribution $P(\phi)$. For the expression given by eq. (1) the width is found to be $\sim$0.3 eV by variational methods. This width will be reduced if the distribution of ϕ becomes sharper around $\phi = 60°, 180°$. The difference in the behavior at the top and bottom of the valence band is due to the nature of the interactions present at the two edges. The bottom of the valence band involves purely σ interactions, while the top involves a mixture of σ and π interactions,

In silicon the bottom of the conduction band in our model is again an invariant of X_1 character as in the crystal, and is thus expected to be a normal edge. In other materials, however, this would not be true.

In addition to dihedral-angle disorder, topological disorder has an important influence on the electronic structure of amorphous semiconductors [8, 9]. The topological disorder manifests itself primarily in the ring statistics of the structure. The presence of odd rings frustrates the possibility of the existence of certain eigenstates and thus has maximal effect near the energies corresponding to those eigenstates. If these energies lie near a band edge, localized states arise at the edge. The eigenstates most affected by the topological disorder are the s-antibonding and p-bonding states. It has been shown [9] that the problem can be reduced to a Lifshitz alloy problem, and an expression for the density of localized states near the edge can be obtained. Again, as in the previous section, we find that the nature of the eigenstates near the band edges in the crystalline state determine the effect of disorder on states near the corresponding edges in the amorphous materials.

The bottom of the valence band being s bonding, is unaffected by topological disorder. Also, the top of the valence band is largely unaffected since π-bonding p functions can be arranged so that topological disorder has no effect on them. The presence of odd rings causes the merging of the lower two peaks in the valence band, and this effect can be used to estimate the concentration of odd rings to be roughly 10%. Using this figure, we find variationally a tail of width $\sim$0.1 eV above a Lifshitz limit at the bottom of the conduction band in silicon from the effect of topological disorder. The overall density of states expected is shown in Fig. 2.

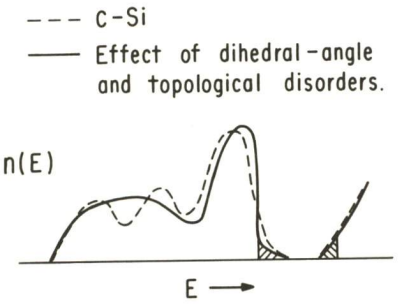

Figure 2 Effect of dihedral-angle and topological disorder on density of states of silicon: Hatched area represents localized states

These results permit an estimate of the mobility gap in a-Si. Ignoring the bond-angle and bond-length disorder gives a band gap equal to that in the crystal, or 1.0 eV. Topological disorder introduces a mobility edge about 0.1 eV up into the conduction band, and dihedral-angle disorder introduces one about 0.3 eV into the valence band. These are shifted apart by about 0.3 to 0.4 eV by the bond-angle disorder. The bond-length disorder is negligible, giving a mobility gap of about 1.8 eV for pure a-Si without coordination defects.

It is clear from the above discussion that both the nature of wavefunctions near the band edges and the magnitude of the disorder are important in determining the tail of width of the tails of localized states. Dihedral-angle disorder can be reduced by adding atoms of an element with a large electronegativity difference from silicon (or another host amorphous semiconductor). This increases the energy barrier between the eclipsed and staggered positions, thus resulting in a narrower tail width at the top of the valence band. For example, the barrier for rotation around Si-F is $\sim$70 meV or ten times as large as that for Si-H.

The odd-even disorder can be suppressed by using III-V compounds [10]. If

coordination defects could be suppressed in these materials, they could give semiconductors with very good conduction band edge. As discussed in a previous section, the ideal material would be one with the bottom of the conduction band near X_1.

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