high-resistance samples shows an extra resistance of few kilohms per 300 kΩ of resistance. If the extra resistance, measured as a function of length, was exponentially dependent on length the observed values are an order of magnitude smaller. Another possibility is to assume that the amount of localization measured in our experiment decreases as the length of the wire decreases. The measuring probes perturb the quantum localization.[13] The smaller the segment the lower the relative value of the extra resistance associated with that segment. If we assume that each probe decreases the extra resistance by a value Δ, the length dependence shown in Fig. 3 can be explained by assuming that Δ is of the order of 0.7 kΩ per probe. This value is comparable to the extra resistance measured as a function of temperature and would suggest that the effect of measuring probes is quite significant.

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# Electronic Structure of Hydrogenated Amorphous Silicon

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Calculations of the electronic states and total energies of various bonding conformations in hydrogenated amorphous Si are presented. Various surprising results emerge, including identification of peaks in photoemission spectra as signatures of *nearest-neighbor* SiH configurations, a gap increasing with increasing H content while the conduction band remains essentially unchanged, and localized states in the gap arising from various defects whose energies are in sharp contrast to recently proposed simple model estimates.

The exciting possibilities of substitutionally doping hydrogenated amorphous Si (*a*-Si:H) and the subsequent construction of a solar cell have inspired a large number of experimental investigations of the structural, electronic, vibrational, and transport properties of this material.[1] Several interesting experimental observations include a much lower mobility for holes than for electrons,[2,3] an optically induced spin signal,[4,5] apparently two peaks in the gap as observed in field-effect measurements,[6] a valence band (VB) which recedes with increasing H content,[7] and photoemission spectra[7] for the high-temperature modification with structure which has been identified as that observed in Si(111):H and Si(100):H. Several theoretical models, including three recent Letters,[8-10] have attempted to explain some of the experimental results in terms of defects or various Si-H bonding conformations. In particular, Fisch and Licciardello[8] have proposed a three-center-bond (TCB) defect with a negative Hubbard $U$; Adler[9] has proposed a simplified bond-strength argument suggesting the double dangling bond as the lowest-energy defect; and Ching *et al.*[10] have calculated the electronic states associated with a number of H-bonding models in a continuous random tetrahedral network (CRTN), indicating that isolated monohydrides are consistent with the photoemission observations.

In this Letter we point out limitations in these theoretical conclusions and attempt to account for all of the experimental observations noted above. Using a Bethe lattice[11,12] (BL) to model the topological disorder of $a$-Si, we present realistic tight-binding and semiempirical total energy calculations to study the electronic structure of various H and Si bonding conformations in $a$-Si:H. Specifically, we find that the similar density-of-states (DOS) structure of monohydrated Si(111) and Si(100) is fortuitous. We show that the $a$-Si:H photoemission measurements are in fact not consistent with Si(111):H or isolated monohydride conformations. The more appropriate conformation appears to be strongly interacting *nearest-neighbor* monohydrides, more closely resembling Si(100):H. We also find that the energy gap increases with increasing H content, predicting a maximum attainable gap of ~3.0 eV. The conduction band, however, remains virtually stationary, suggesting a large anisotropy between electron and hole mobilities, as measured experimentally.[2,3] We find in addition that the lowest-energy defect in the system is evidently neither a single dangling bond nor Adler's[9] recently proposed double dangling bond. One lower-energy defect is a relaxed dimer; this pairs electrons and can account for the optically induced EPR signal observed in silane-decomposed[4] and sputtered[5] samples. We also find that the total energies of two TCB conformations indicate that H atoms may be able to bond to normally coordinated Si atoms. Both conformations provide states in the gap, but only one state has H-like character. We show that a negative $U$ for the TCB is unlikely because of electron localization and Coulomb repulsion between the monohydride and dangling bond.

The tight-binding Hamiltonian that we use includes all nearest-neighbor interactions between the valence orbitals on each atom.[12,13] These interactions are fitted to bulk crystalline Si and gaseous silane energy states with no further empirical adjustment. To simulate the structure of an amorphous network we use the cluster-Bethe-lattice method.[11,12] We assume that the $a$-Si network can be modeled by a Si BL, which contains no ring statistics but which describes the VB structure of the selvedge region measured in photoemission experiments fairly well.[12] Total energies are calculated by summing one-electron energies and including an additional repulsive term per bond. This term corresponds to ion-ion repulsion and corrections for the over counting of electron-electron interactions. It is very difficult to calculate exactly, but can be estimated empirically by fitting to solid and molecule bond dissociation energies.[14] This is a very important correction that has been neglected in previous studies.

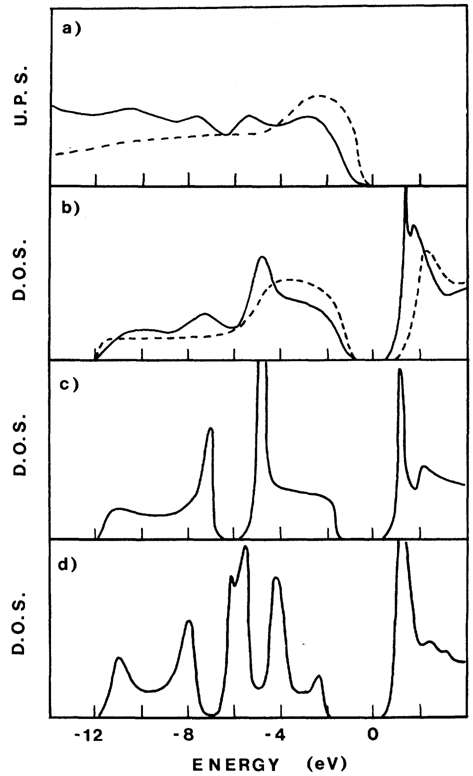


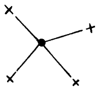
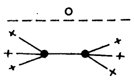
FIG. 1. (a) UPS measurements (Ref. 7) for $a$-Si (dashed line) and $a$-Si:H (solid line). (b) Theoretical DOS for $a$-Si modeled by Si Bethe lattice (dashed line) and DOS for $a$-Si:H modeled by a cluster of adjacent monohydrides with Si Bethe lattices attached to dangling bonds (solid line). (c) DOS for monohydride Bethe lattice. (d) DOS for polysilane.

In Fig. 1(a), we show photoemission spectra[7] ($\hbar\omega = 40.8$ eV) obtained for sputtered *a*-Si and *a*-Si:H. The only H bonding consistent with this spectrum is monohydride,[7,13] because of the single peak near − 5.0 eV which is well known in the study of hydrogenated Si(111) surfaces.[15] The peaks at − 5.0 and − 7.5 eV were originally compared with Si(111):SiH calculations[15] (Fig. 2 of Ref. 7). The peak near − 10.5 eV, which was not discussed in the original experiment,[7] also seems consistent with this interpretation. These same peaks have also been compared with similar structure in the CRTN calculations of Ching *et al.*[10] on *a*-Si:SiH. We wish, however, to point out the speciousness of these comparisons. At energies below about − 6.0 eV, structure seen in the DOS of weakly interacting monohydrides arises primarily from the local ring topology of the Si atoms to which the H is bonded. [For example, the peaks near − 7 and − 10 eV in Si(111): H calculations[16] derive from sixfold rings near the surface.] This structure is therefore *not* an intrinsic property of the Si-H bond and in fact vanishes in the DOS calculated for a single monohydride in a BL.[13] The monohydride calculation of Ref. 10 does nothing to incorporate *local* topological disorder, and hence the multipeak structure obtained is questionable for *a*-Si:H. A disordered Si network with varying ring statistics would show no discernible peaks in this energy regime, as is evident in the *a*-Si spectrum in Fig. 1(a). We conclude, after considering a large variety of *a*-Si:H bonding conformations,[17] that structure seen near − 7.5 and − 10.5 eV in the hydrogenated spectrum is consistent with only *nearest*-neighbor monohydride configurations.[18] This is shown in Fig. 1(b) where we compare our calculations for the DOS of a Si BL with that of a coupled monohydrated Si bonding conformation. We note that the trends observed in the experimental and theoretical curves are quite similar.

To investigate the behavior of the energy gap of *a*-Si:H with H content, we compare the solid line in Fig. 1(b) with the results in Figs. 1(c) and 1(d). Here we have calculated the DOS of a SiH BL and a polysilane $(SiH_2)_n$ structure, respectively. The results show that the VB maximum recedes rapidly with increasing H content, consistent with photoemission measurements.[7] It is surprising, however, that the CB edge does not change appreciably, suggesting that local H-content fluctuations in *a*-Si:H can create localized states near the VB edge. The number of these states may be quite large (~ $10^{20}$ cm$^{-3}$) and could explain the elusive $E_y$ peak observed in field effect measurements.[19] Moreover, these states would act as deep traps for holes and thus provide a natural explanation for the large disparity between hole and electron mobilities observed in these materials.[2,3] Finally, we note that the results in Fig. 1(d) also predict that the maximum attainable gap in *a*-Si:H is ~ 3.0 eV, corresponding to a fully polysilanated structure.

Let us now investigate the role of defects in interpreting the EPR measurements,[4,5] which find no equilibrium spins and an optically induced spin density ~ $10^{17}$–$10^{18}$. The results of our calculations for one-electron ($E_{\rm el}$) and total ($E_{\rm tot}$) energies are summarized in Table I. The corresponding one electron DOS for these defects are shown in Fig. 2. In Fig. 2(a) we show the DOS for threefold-coordinated ($T_3^0$) and relaxed twofold-coordinated ($T_2^0$) Si defects. We notice that the $T_2^0$ has two states in the gap, the upper one of which is empty. Thus the $T_2^0$ could act as an electron or hole trap as suggested recently by Adler.[9] We see from Table I, however, that the total energy of a $T_3^0$ is most likely lower than that of the $T_2^0$, in contrast to earlier estimates.[9]

TABLE I. One-electron ($E_{\rm el}$) and total ($E_{\rm tot}$) energies of indicated defects. The energies on the left panel are referred to a normally coordinated Si atom in the Bethe lattice. The energies on the right panel are referred to an isolated H atom and two normally coordinated Si atoms in the Bethe lattice. The dashed lines denote isolation of defects. Error limits reflect the range of measured bond energies used in fitting $E_{\rm tot} - E_{\rm el}$.

| REFERENCE  | ●: Si ○: H | | REFERENCE  | +: Bethe Lattice | |
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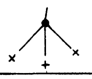
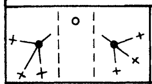
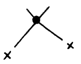
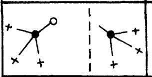
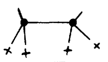
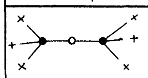
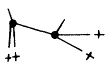
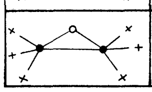
| | $E_{el}$ | $E_{tot}$ | | $E_{el}$ | $E_{tot}$ |
|  | 3.4 | 1.4±0.1 |  | 6.7 | 2.8±0.2 |
|  | 5.5 | 1.6±0.3 |  | -1.0 | -1.2±0.6 |
|  | 3.1[a] | 1.2±0.1[a] |  | -3.5 | -0.7±0.5 |
|  | 2.9[a] | 0.9±0.1[a] |  | -5.7 | -0.2±0.4 |

[a] Per defect atom.

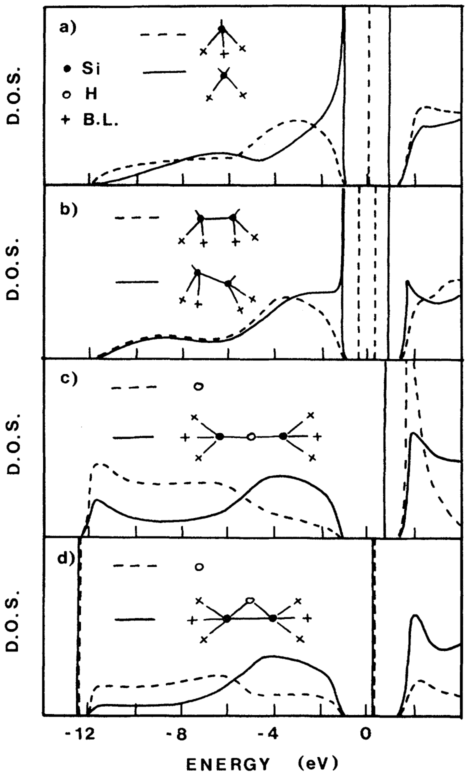


FIG. 2. Theoretical local DOS for the various defect atoms shown schematically in each panel with Si Bethe lattices attached as indicated. (a) Neutral threefold-coordinated ($T_3^0$) and relaxed twofold-coordinated ($T_2^0$) Si defects. (b) Unrelaxed dimer (dashed line) and relaxed dimer (solid line). (c) Linear TCB (solid line) and local DOS on its H atom (dashed line). (d) Bridging TCB (solid line) and local H DOS (dashed line) showing H character in gap state.

Table I also reveals that there may exist an even lower-energy Si defect (ignoring any entropy considerations). This defect is comprised of nearest-neighbor $T_3^0$ making a dimerlike configuration. In the relaxed form, we consider the extreme case where one atom makes $sp^2$ bonds and transfers its electron to the other atom forming $p^3$ bonds. In Fig. 2(b) we show our results for the DOS of both unrelaxed and relaxed dimerlike configurations. The solid and dashed curves thus reveal the range of possible energies of these defect states caused by disorder and steric constraints. We also note that these defect states could act as traps for optically induced electrons and holes as observed experimentally.[4,5]

By analogy to diborane bonding, TCB's have recently been proposed[20] as an important H bonding conformation in *a*-Si:H. Indeed, Table I indicates that TCB's may be stable with respect to *isolated* H atoms and normally coordinated Si atoms. Here we consider a linear TCB and a bridging TCB. We find that these TCB's have similar total energies but have states in the gap of markedly different character. This is shown in Figs. 2(c) and 2(d). In particular, the gap state in Fig. 2(c) is a purely Si antibonding state containing one electron. Thus this state would persist even in the absence of H, but would then be empty. The gap state in Fig. 2(d), however, is a Si-Si bonding, Si-H antibonding state containing one electron. The large H character in this state would predict a hyperfine contribution to EPR that does not seem to be observed experimentally. It is interesting to note that this state actually originates from the conduction-band edge of Fig. 2(c). Similarly, the gap state in Fig. 2(c) originates from the conduction-band edge of Fig. 2(d). One would therefore expect that at intermediate geometries these states would cross. Finally, it has been suggested that the linear TCB may have a negative effective Hubbard $U$ by capture of an electron and decay into monohydride and $T_3^-$.[2] We argue against a negative $U$ for basically three reasons. First, our calculations indicate a net charge transfer to the H atom in a monohydride; this will result in a repulsive "H bond" with the $T_3^-$. Second, the correlation energy will *increase* due to increased localization of electrons in the dangling bond. Finally, the existence of an important negative-$U$ defect remains unlikely since the Fermi level is not pinned.

All of the defects considered here exhibit a common feature of clustering states at a characteristic energy of about 0.6 eV below the conduction-band edge. It is possible that some of these states may correspond to the $E_x$ peak observed in field-effect measurements.[6]

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[18] We have argued that only nearest-neighbor SiH's can account for the structure below − 6 eV when topological constraints are relaxed. If there are many second-neighbor SiH's, however, a qualitatively similar structure is observed, for example, in the DOS calculation of Si(111):H with relaxed topology [F. Yndurain and E. Louis, Solid State Commun. 25, 439 (1978)]. The *quantitative* results, however, are very sensitive to the Hamiltonian, and we have found that calculations on Si(111):H with relaxed topology using Pandey's realistic Hamiltonian (including second-neighbor interactions, Ref. 16) give quantitative results which do not agree with the more approximate Hamiltonian of Yndurain and Louis nor with experiment for *a*-Si:H.

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# Resolution of Shubnikov–de Haas Paradoxes in Si Inversion Layers

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In two dimensions the frequency of magnetoconductivity oscillations measures the sum of Fermi-surface areas when the Landau levels are sharp. This explains why (100) Si inversion layers with two occupied subbands show only one frequency. It also explains why the frequency observed on (111) surfaces simulates a valley degeneracy of 2, even though six valleys are occupied.

In a recent experiment by Stallhofer, Kotthaus, and Abstreiter[1] it was shown that in Si(100) inversion layers under uniaxial stress two masses could be observed corresponding to simultaneous occupation of both subbands $E_0$ and $E_{0'}$. However, in a subsequent experiment by Gesch *et al.*,[2] in which cyclotron resonance and Shubnikov–de Haas (SdH) oscillations were observed on the same sample and under identical conditions, the oscillations showed only one frequency corresponding to all the electrons. One would have expected a superposition of two frequencies. In this Letter we show that this apparent discrepancy is to be expected in a two-dimensional system with sharp Landau levels. In the same way the long-standing problem of the unexpected (apparent) twofold valley degeneracy on (110) and (111) surfaces[3-7] can also be understood without resorting to an extremely high strain at the surface.[5]

On the (100) surface the electrons in the inversion layer are quantized into two different types of subbands[8]: The two valleys of the conduction band of Si that have their longitudinal mass perpendicular to the surface give rise to one set of subbands $(0, 1, 2, \ldots)$ which has a small effective mass $m = 0.19m_e$ for motion parallel to the surface. The other four valleys give rise to another set $(0', 1', 2', \ldots)$ which has a greater mass $m' = 0.42m_e$. Usually, only subband 0 is occupied, but application of uniaxial stress can move two of the four other valleys down in energy, so that the 0′ subband gets populated. Furthermore, a magnetic field applied perpendicular to the surface causes the subbands to quantize into Landau