

Theoretical Studies of Electronic States Produced by Hydrogenation of Amorphous Silicon

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First-principles calculations of electronic energies of hydrogenated amorphous silicon have been performed for a series of realistic structural models in which hydrogen appears as SiH, SiH₂, SiH₃, (SiH₂)₂, and SiHHSi (a broken Si-Si with two H atoms). Whereas all these models are consistent with photoemission experiment (less so for SiH₃), only the last two are found to give band-gap states. The broken-band model is in good agreement with several sets of experiments.

Recent demonstrations of drastic changes in the properties of amorphous silicon (*a*-Si) by hydrogenation have stimulated many experimental studies.¹ The H atoms tie off the dangling bonds and greatly reduce the gap states. At low concentrations the H atoms may be expected to bond in the monohydride (SiH) form.^{2,3} However, photoconductivity measurements on samples with different H contents suggest that gap states near the conduction-band (CB) edge are produced at high densities of H atoms.⁴ Also observed are changes in photoemission and infrared vibration spectra at increasing H concentrations.³⁻⁵ To explain such variations, several structural units have been proposed, but considerable disagreement exists regarding their relative importance. Brodsky *et al.* suggested SiH, SiH₂, and SiH₃,² whereas (SiH₂)_n was given preference to SiH₃ by Knights, Lucovsky, and Demanich.³ Among the SiH_n units, von Roedern *et al.* argued that the dihydride is relatively unimportant,⁵ yet Freeman and Paul found evidence for SiH₂ but none for SiH₃.⁶ They also indicated the possibility of two different kinds of SiH units.⁶ Furthermore, observation of two characteristic temperatures in H effusion experiments led to the suggestion of SiH and SiH₂.⁷

The lack of reliable, first-principles calculations of electronic states of hydrogenated *a*-Si had made it difficult to interpret fully some of the experimental results and to utilize them for elucidating bonding structure. Thus we have performed first-principles calculations of electronic energies using several realistic continuous-random-tetrahedral-network (CRTN) structural models of *a*-Si which contain different bonding

configurations with hydrogen. For model construction, we hand built an *a*-Si CRTN (about 170 atoms) containing one particular configuration unit (say SiH₂) in the middle, followed by computer relaxation based on Si-Si stretching and Si-Si-Si, Si-Si-H, and H-Si-H bending force constants.³ The Si-H distance was kept at 1.48 Å (bond length of SiH₄) throughout. With a given hydrogenated CRTN, we generate the one-electron Hamiltonian by a superposition of atomic potentials (statistical exchange) at each site and solve for the energies by the method of orthogonalized linear combinations of atomic orbitals (OLCAO) with a cluster-type basis set covering the 1s orbital of H and the 3s and 3p orbitals of some 34 Si atoms which are orthogonalized to the 1s, 2s, and 2p cores of all Si atoms in the CRTN. Application of this *ab initio* OLCAO method (with cluster basis) to intrinsic *a*-Si has been described in detail elsewhere.⁸ To test the potential, we performed a similar calculation for SiH₄ and the energy levels obtained agreed well with other calculations⁹ and with photoionization measurements.¹⁰

To each electronic wave function derived from a hydrogenated CRTN, we apply Mulliken's population analysis¹¹ to determine the fraction of electron charge associated with the H atoms from which we obtain the local density of states (LDS) at the H atoms. The results for the SiH, SiH₂, and SiH₃ configurations are displayed in Fig. 1. A Gaussian broadening (half-width 0.5 eV) has been applied. In the valence-band (VB) region, the SiH configuration [Fig. 1(a)] gives a major peak at -7 eV ($E=0$ at VB top), whose wave functions exhibit Si(3p)-H(1s) bonding characters.

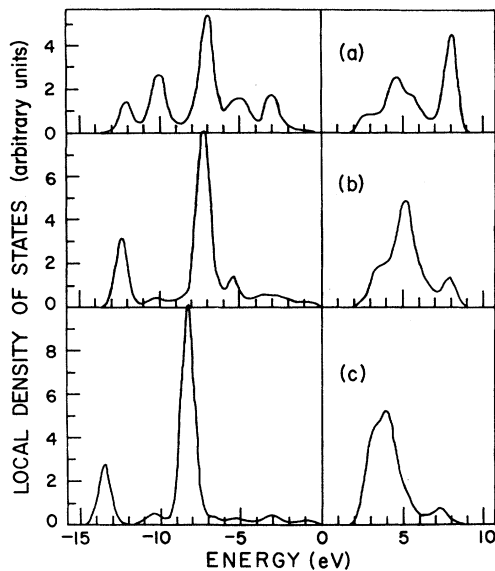


FIG. 1. Calculated hydrogen LDS for α -Si containing (a) SiH, (b) SiH₂, and (c) SiH₃.

This peak is in reasonable agreement with the observed photoemission peak at -6 eV which shifts to -6.3 eV at higher H concentration.⁵ There are four other peaks of considerable strength; the last two (-10 , -12 eV) involve mainly Si(3s) bonding states. The multiplex structure indicates permeation of the H orbital into many VB states through its interaction with nonadjacent Si atoms. For the cases of SiH₂ and SiH₃ [Figs. 1(b) and 1(c)], only one prominent peak (-7.3 eV for SiH₂ and -8.2 eV for SiH₃) for the p -bonding states and one (-12.4 and -13.5 eV, respectively) for the s states are seen. The sharpening of peaks in going from SiH to SiH₃ indicates a reduction of the interaction of H with nonadjacent Si atoms. In spite of the shift of individual peaks, the peak separations for SiH₂ (5.1 eV) and SiH₃ (5.3 eV) are nearly equal and are in good agreement with the 5.0-eV "A-B splitting" observed by von Roedern *et al.*⁵ These authors rule out SiH₂ as a main contributor because they infer from the experimental data of SiH₂ adsorbed on Si(100) surfaces that the A-B splitting of SiH₂ is about 1.6 eV.¹² However, as adsorbate on Si(100), the nearest distance from an H in one SiH₂ to an H in the next unit is much smaller than the H-H separation within an SiH₂ unit.¹² Thus Si(100):SiH₂ may show quite different behavior from α -Si:SiH₂. According to Fig. 1(b), we see that SiH₂ is consistent with the photoemission data of Ref. 5. For the CB we notice in Fig. 1 a downward shift of the hy-

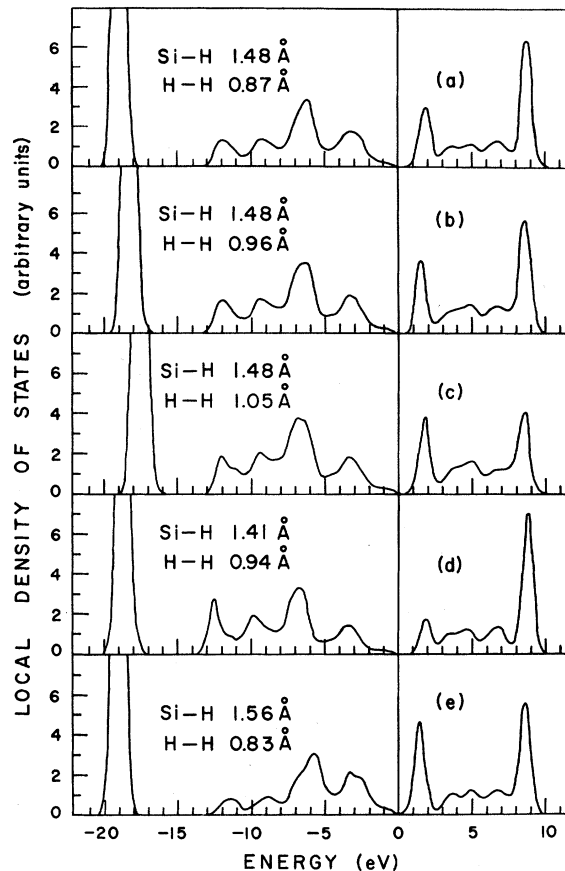


FIG. 2. Calculated hydrogen LDS for five broken-bond models with parameters given in the figure.

drogen LDS peak from SiH to SiH₃. These states can be characterized as Si-H antibonding states, but the s and p orbitals of the bonded Si atom are generally quite mixed. All three kinds of SiH_{*n*} yield no gap states.

We next examine a broken-bond (BB) model in which two H atoms are inserted in a broken Si-Si bond to form a SiHHSi complex in an α -Si CRTN. Taking the H-H distance as 0.87, 0.96, and 1.05 Å for three different models with a fixed Si-H length (1.48 Å), we display their hydrogen LDS in Figs. 2(a)-2(c). The most obvious new features are the gap states and the large peak at ~ -18 eV. To explain them let us denote a bonding and an antibonding orbital of Si-H as SiH^b and SiH^a, respectively. The peak at -18 eV arises from the bonding of one SiH^b orbital (in which the Si function is primarily s type) with the other within an SiHHSi complex. Examination of the wave functions indeed reveals a concentration of charge density between the two H atoms. Likewise we attribute the gap states to those with bonding

combinations of two SiH^a orbitals. For a single SiH in a CRTN, the SiH^a -type states are in the CB, but with SiHHSi the interhydride bonding pushes the SiH^a states to the gap. For the three BB models in which the H-H distance varies over 20% with a fixed Si-H length, the gap-state distribution remains quite similar, but the “-18-eV peak” moves by 1.5 eV. If we strengthen the Si-H bond by shortening it, the energy shift due to H-H interaction would be lessened resulting in a rarefaction of gap states. This is confirmed by a calculation [Fig. 2(d)] using 1.41 Å for the Si-H distance. Conversely increasing the Si-H distance to 1.56 Å enlarges the gap-state peak as illustrated in Fig. 2(e).

The appearance of gap states due to interhydride bonding motivates us to study three models containing SiH_2 - SiH_2 with Si-Si distance covering 2.25 [Fig. 3(a)], 2.02, and 2.48 Å [Fig. 3(b)]. The gap states in Fig. 3(a) indeed arise from such a bonding interaction. They are not as conspicuous as the ones in Fig. 2 because of the more distant separation of H atoms in $(\text{SiH}_2)_2$. The extra peak [as compared to Fig. 1(b)] at the lower end of the VB (-14 eV) is a manifestation of interhydride bonding, analogous to the “(-18)-eV peak” in Fig. 2. The interhydride bonding intensifies upon con-

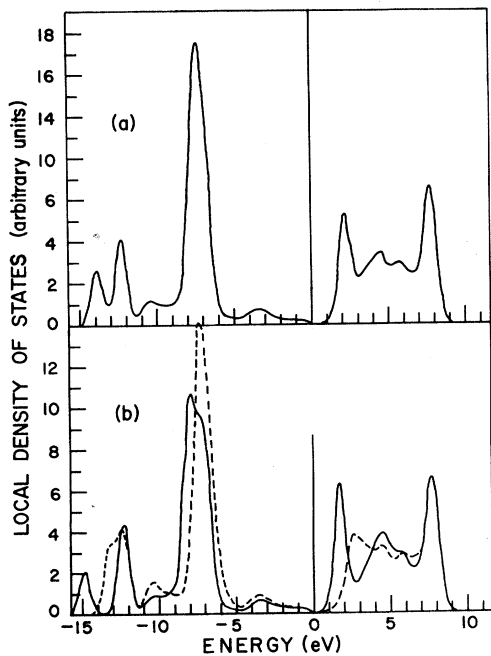


FIG. 3. Calculated hydrogen LDS for the SiH_2 - SiH_2 model with Si-Si distance equal to (a) 2.25 Å, (b) 2.02 Å (solid curve), and 2.48 Å (dashed curve).

tracting the Si-Si bond. Thus at a shorter Si-Si distance, the gap states are better developed and the bottom VB peak more distinct, whereas the trend reverses when the Si-Si bond is lengthened [Fig. 3(b)].

Our electronic energy calculations afford an effective means toward identifying H-bonding configurations. Both the SiH and SiH_2 models (especially SiH_2) give VB energies in reasonable accord with the photoemission data.⁵ The experimental shift of the p -bond peak by ~ 0.3 eV at elevated H concentrations⁵ is well reproduced in Figs. 1(a)-1(b). The much larger p -peak shift calculated for SiH_3 in Fig. 1(c) renders the trihydride less favorable as a major configuration. We find no gap states when only isolated units of SiH_n are present. On the other hand, the BB and $(\text{SiH}_2)_2$ models do give gap states, and hence can be used to explain the formation of gap states near the CB edge by hydrogenation at increasing concentrations. Particularly the BB model appears to be an attractive candidate. It implies a relatively easy effusion of H in the form of H_2 which may account for the lower characteristic temperature observed experimentally.⁷ This model is also consistent with the presence of two different kinds of SiH units suggested by Freeman and Paul.⁶ Furthermore the BB model provides a simple mechanism for incorporating H atoms to quite high concentrations. Based on Figs. 2(a)-2(c), we expect that for H-H distance well above 1.05 Å, the gap states would still persist but the “(-18)-eV peak” may move upward considerably. A series of test calculations indicates that the qualitative features of the LDS are not sensitive to the atomic positions in the CRTN and the potential used in the OLCAO calculations.¹³ Experimental investigation of photoemission spectra near and below the bottom of the VB should be valuable. To model hydrogenated α -Si, one would place units such as SiHHSi all over the CRTN. The interaction between two SiHHSi units, even when placed in the nearest possible position, would not significantly alter the valence-band gap-state LDS, because the interunit H-H distances are much larger than the intraunit ones. Thus calculations based on single units do provide a realistic picture. We have examined several other configurations including an interstitial H, and H at the middle of a six- (or five-) member Si ring, and SiHSi bridges¹⁴ of various geometrical forms. The calculated VB LDS are all drastically different from Figs. 1-3 as well as from the photoemission data, and will not be presented here.

A detailed analysis of the results for the various models will be given in a forthcoming paper.

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¹⁴The SiHSi bridge model has been discussed recently by R. Fisch and D. C. Licciardello, *Phys. Rev. Lett.* **41**, 889 (1978). For this model we found one gap state at 0.7 eV which has virtually zero charge density at the H site.

Quadrupole Splitting of Muonium Precession in α -Quartz

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Muonium-spin-rotation experiments at low fields (< 75) show evidence for the interaction of the interstitial charge distribution of crystalline quartz with the intrinsic electric quadrupole deformation of the triplet ground state of the muonium atom.

The first direct observation of triplet ($F = 1$) muonium (Mu) precession in a solid was achieved in 1968 using positive muons stopped in fused quartz (SiO_2) in a 7.2-G magnetic field.¹ The apparent relaxation rate of the Mu polarization was seen to be faster in crystalline SiO_2 than in fused SiO_2 . Since then, fused SiO_2 has been routinely used to calibrate the efficiency of other materials for Mu formation—the μ^+ has a higher probability of forming Mu in SiO_2 than in any other known solid. Fused quartz was also the first medium in which “two-frequency precession” of Mu was observed² in magnetic fields ≥ 50 G. This phenomenon, due to a quadratic Zeeman term in the energy of the $M = 0$ states, has been used to measure the strength of the Fermi contact inter-

action between μ^+ and e^- spins in the strongly coupled “deep” Mu atom in SiO_2 , Ge, and Si.²⁻⁴ This interaction is normally isotropic, but in Si crystals a dramatic anisotropy has been observed in the phenomenological hyperfine interaction of a second, weakly coupled, “shallow” Mu* (anomalous muonium) state.⁵

We have now observed a new phenomenon: The precession of triplet Mu in a quartz crystal is split into two clearly resolved frequencies whose difference is as large as 0.79 MHz in an applied field of 3.3 G, where the usual splitting due to the quadratic Zeeman effect should be only 0.0047 MHz. Moreover, the splitting is independent of field strength but depends dramatically upon the orientation of the crystal in the field. As we