Electronic states and bonding configurations in hydrogenated amorphous silicon

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A series of realistic structural models have been constructed for hydrogenated amorphous silicon (a-Si:H) with the hydrogen atoms appearing as SiH, SiH$_2$, SiH$_3$, (SiH$_2$)$_2$, SiHHSi (a broken Si–Si bond with two H atoms inserted), SiHSi (bridge form), an interstitial atom, and an atom at the center of a six-member ring (ring-center model) in an otherwise continuous-random-tetrahedral network of amorphous silicon. The electronic energies for each structural model (with one H-bonding configuration) are calculated by using the first-principles method of linear combinations of atomic orbitals in which all the multicenter integrals in the Hamiltonian matrix elements are evaluated exactly. In the cases of the SiH, SiH$_2$, SiH$_3$, SiHHSi, and (SiH$_2$)$_2$ configurations, the calculated local densities of states of the valence band for the H atoms agree well with photoemission experiment, but a distinct discrepancy is found for the SiHSi bridge model and the ring-center model. The SiHHSi and (SiH$_2$)$_2$ models give gap states near the conduction-band edge, the occurrence of which is attributed to the interhydride interaction. The SiHHSi model is in good agreement with several sets of experiments and provides a simple mechanism for incorporating H atoms in amorphous Si to fairly high concentrations.

I. INTRODUCTION

The successful demonstration[1] that amorphous silicon (a-Si) prepared by glow discharge in silane gas can be doped to exhibit n-type or p-type behavior has stimulated many experimental studies[2] on the properties of hydrogenated a-Si (a-Si:H). Recently such doping is also found possible for a-Si:H samples prepared by rf sputtering.[3] It is generally assumed that one important function of the H atoms is to act as a terminator of the dangling bonds present in the a-Si sample due to structural defects, thereby removing most of the gap states. However, experiments show that hydrogen can enter a-Si films up to more than 30 at.%, far in excess of the estimated concentration of dangling bonds.[4-7] Furthermore, even for highly hydrogenated samples, there still remain appreciable electron-spin-resonance (ESR) signals, indicating the presence of unpaired electrons.[8]

One important step toward understanding the properties of a-Si:H is to determine how the H atoms are bonded to the Si atoms in the sample. At low H concentrations, one may expect the H atoms to be mainly in the monohydride from (SiH).[5,6,9] For samples containing higher densities of H atoms, other structural units may also be present, and considerable disagreement exists regarding their relative importance. Brodsky, Cardona, and Cuomo suggested the presence of

SiH, SiH$_2$, and SiH$_3$ units,[5] whereas Knights, Lucovsky, and Nemanich[6] concluded that the majority of the H atoms appear as short (SiH$_2$)$_n$ chains. More recently Freeman and Paul[9] found evidence for SiH$_2$ but no evidence for SiH$_3$. They also indicate the possibility of two different kinds of SiH units.[9] Furthermore, observation of two characteristic temperatures in H effusion experiments led to the suggestion of SiH and SiH$_2$ units.[10] Von Roedern *et al.*[7,11] found two different photoemission spectra depending on the method of preparation of samples and suggested different H-bonding configurations for each kind. Closely related to the question of bonding configuration is the observed shift of photoconductivity edge with increasing H concentration, which is suggestive of the presence of SiH antibonding states near the bottom of the conduction band (CB).[12]

Because of the enormous complexity of a disordered system such as a-Si:H with regard to the microscopic structure, very little theoretical work based on first-principles calculation of the electronic energies has been done. The lack of such theoretical calculations for a-Si:H made it difficult to interpret fully the experimental results and to utilize them for elucidating bonding structure. In recent years we have adopted the method of linear combinations of atomic orbitals (LCAO) for first-principles calculation[13,14] of electronic energy of a-Si. With a given set of the atomic positions for a continuous-random-tetrahedral-

network (CRTN) structural model of a-Si, we construct the potential by a superposition of the atomic potentials at all sites, so that the detailed structural disorder is fully represented in the Hamiltonian in a realistic way without using any empirical parametrization. The electronic energies are then determined by the LCAO method with all the multicenter integrals evaluated exactly. This method has been applied to the case of intrinsic a-Si to calculate the electronic energy structure[13,14] and the optical dielectric function[15] with good agreement with experiment.

In this paper we report a theoretical study of the electronic states of a-Si:H. Our first step is to build a number of CRTN structural models for a-Si:H assuming different bonding configurations between H and Si. The LCAO method is then applied to obtain the electronic energies. Comparison of these results with experimental data provides an effective means of identifying H-bonding configurations in the a-Si:H samples. A brief account of some of the preliminary results has been presented in Ref. 16.

II. STRUCTURAL MODELS

The H-bonding configurations considered in this paper include the following:

(a) monohydride, SiH;

(b) dihydride, SiH_2;

(c) trihydride, SiH_3;

(d) broken-bond (BB) model, a broken Si–Si bond with two H atoms inserted, SiHHSi;

(e) $(SiH_2)_2$, a special case of the polymeric form $(SiH_2)_n$;

(f) bridge model, SiHSi;

(g) ring-center model, H atom at the center of a six-member ring;

(h) interstitial H atom.

To construct structural models, we first hand-build an a-Si CRTN (with 140–230 atoms) containing a particular configuration unit. Except as otherwise noted, the Si–H bond length is fixed at 1.48 Å, the silane bond length. The coordinates of the H and Si atoms are measured and subsequently relaxed by computer, as guided by an elastic potential similar to the Keating form[17] with Si–Si stretching and Si–Si–Si, Si–Si–H, and H–Si–H bending force constants.[6] One could equally as well generate the structural models entirely by computer, but we find it more expedient to construct the model initially by hand. Also the hand-built model gives a clear visual perception of the geometrical arrangement of the atoms around H. For instance, we notice that for models containing an SiH_n unit (with no other in-

ternal defect), there is always a "cavity" surrounding the H atoms. The size of this cavity increases as one moves from SiH to SiH_3 with corresponding increase in strain. A two-dimensional schematic illustration is given in Fig. 1.

III. METHOD OF CALCULATION

The LCAO method as applied to amorphous solids has been described in the literature.[13–15] Only a brief outline will be given here. The basis functions consist of optimized Si $1s, 2s, 2p, 3s, 3p$ atomic wave functions[18] and H $1s$ functions which are all expanded by the Gaussian-type orbitals (GTO).[19] The valence orbitals ($3s, 3p$ for Si and $1s$ for H) at each site are orthogonalized to the core orbitals ($1s, 2s, 2p$ of Si) of all other atoms so that the latter can be deleted from the basis set.[13,20] The Hamiltonian is generated by taking a superposition of the atomic potentials (using the statistical exchange approximation), i.e., the overlapping-atomic-potential (OAP) approximation. Since the electronic-energy calculation is not carried out to self-consistency, it is important to have an independent check on the individual atomic potentials used. To this end we computed the electronic energies of the SiH_4 molecule using a similar OAP approximation for the potential and the same atomic basis functions, and obtained the energies of the occupied A_1 and T_2 levels as -19.2 and -13.1 eV, respectively, in good agreement with experimental ionization-potential measurements[21] and also with other theoretical calculations.[22]

A CRTN contains typically 200 atoms with the H atoms in the middle. The potential term in the Hamiltonian includes the contributions from all these atoms. The basis functions, however, are confined to 35–40 atoms near the center of the CRTN. The use of such cluster-type basis functions in conjunction with a Hamiltonian for a much
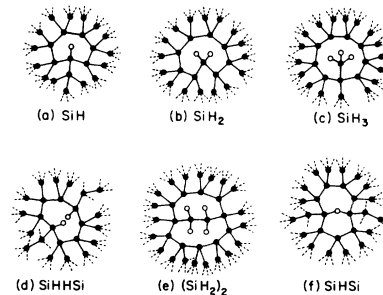

FIG. 1. Two-dimensional sketches (not drawn to scale) of structural models for a-Si:H with six different H-bonding configurations as indicated. The H atoms are denoted by hollow circles, and Si by solid circles.

larger lattice has been discussed in earlier papers,[13,23,24] and this scheme has been applied successfully to perfect crystals,[23] point-defect crystal systems,[24] and amorphous Si.[13,14] In this manner one can extend the LCAO method to non-periodic solid systems with secular equations within a manageable size. By means of the Gaussian technique, all the multicenter integrals in the kinetic and potential terms are evaluated exactly.[13,14] In this work all the matrix elements are taken into account, and no approximation, such as neglecting integrals involving distant neighbors, need be made. Solution of the secular equation gives the electronic energies and wave functions. Because the basis functions do not overlap the boundary atoms of the CRTN, no spurious surface states appear in our solution. A Gaussian broadening of half-width 0.5 eV has been applied for calculating the density of states (DOS). To each electronic wave function we use Mulliken's population analysis[25] to determine the fraction of electron charge associated with the H atoms. Applying this weighting factor to the DOS, we obtain the local density of states (LDS) of the H atoms (H-LDS). Those Si atoms that are bonded to H are of special interest, and are designated, in this paper, as Si*. Analogous to H-LDS, we compute the LDS associated with the Si* atoms (called Si*-LDS). Moreover we can resolve the Si*-LDS into a component for the 3p orbitals and one for the 3s in order to examine the nature of the Si–H bond. We have tested the adequacy of our basis set by enlarging the cluster within which our basis functions are located. This was performed for the specific case of the SiH configuration. The calculated H-LDS is found to be extremely insensitive to such a change as one would expect, since the additional functions, being far away from the SiH unit, have little influence on the H-LDS.

IV. RESULTS AND COMPARISON WITH EXPERIMENT

In this section we present the calculated LDS for a series of a-Si:H CRTN containing a single unit of the kind listed in Sec. II, and compare the results with the experimental photoemission data. As a reference for comparison, we use the procedure outlined in the preceding section to compute the DOS for the CRTN model of pure a-Si given by Polk and Boudreaux[26] and subsequently refined by Steinhart, Alben, and Weaire[27] (referred to as the RPB CRTN). This is shown in Fig. 2 which agrees well with our earlier, more elaborate calculation for the same CRTN.[13,28]

A. Isolated hydrides

The simplest bonding pattern between H and Si is that of hydrides, SiH, SiH_2, and SiH_3. Forma-

tion of hydrides has the effect of eliminating dangling bonds which may explain the reduction in ESR signal for a-Si samples prepared by glow discharge decomposition of silane. Evidence for the hydride configurations has been reported in the literature from different laboratories,[5-11] but there appears to be no consensus on the relative importance of the three forms.

In Fig. 3(a) we display the H-LDS of the valence band (VB) and CB for the SiH configuration. We have also examined the 3s and 3p components of the Si*-LDS which are shown in Figs. 3(b) and 3(c), respectively. The major peak for the H-LDS of the VB occurs at -7.0 eV (the top of the VB being taken as zero). From the corresponding structure in Fig. 3(b), it is clear that this peak is due to the Si$3p$–H$1s$ bonding states. There are also four other peaks of considerable strength at -12.1, -10, -5.1, and -3.0 eV. Inspection of Figs. 3(b) and 3(c) shows that the two peaks at -12.1 and -10 eV are associated with Si$3s$–H$1s$ bonding and the other two with Si$3p$–H$1s$. The multipeak structure indicates permeation of the H orbitals into many VB states through the interaction of the hydride group with the other Si atoms in the cluster. The CB states in Fig. 3(a) are generally antibonding with respect to Si–H. As to the Si* orbitals involved, most of the states have mixed s and p character, except for the ones near the top of the CB which are of p-type. No gap states are found.

For the case of the SiH_2 configuration, the H-LDS and Si*-LDS (s and p component separately) are shown in Figs. 4(a)–4(c). The corresponding graphs for the SiH_3 configuration may be found in Fig. 5. Here we see only one prominent peak (-7.3 eV for SiH_2 and -8.2 eV for SiH_3) for the Si$3p$-bonding states and one (-12.4 and -13.5 eV, respectively) for the Si$3s$-bonding states in the VB. The separation of the two VB peaks for
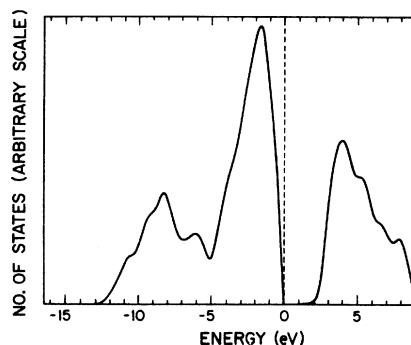

FIG. 2. Density of states of the valence and conduction bands of a-Si based on the RPB CRTN and calculated by using the method described in Sec. III.
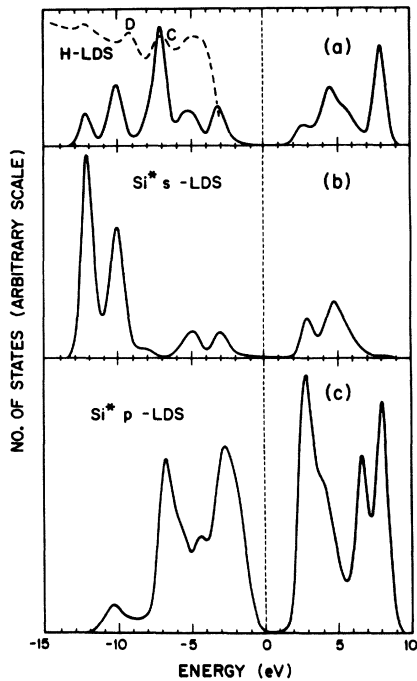
FIG. 3. The solid curves are local density of states of the valence and conduction bands of a-Si containing an SiH unit: (a) LDS of the H atom, (b) the 3s component of the LDS of the Si atom attached to H, (c) the 3p component of the LDS of the Si atom attached to H. The photoemission data (C-D-type) of Ref. 7 are included in (a) as a dashed curve with a shift in energy to match peak C of their data to our calculated central peak.
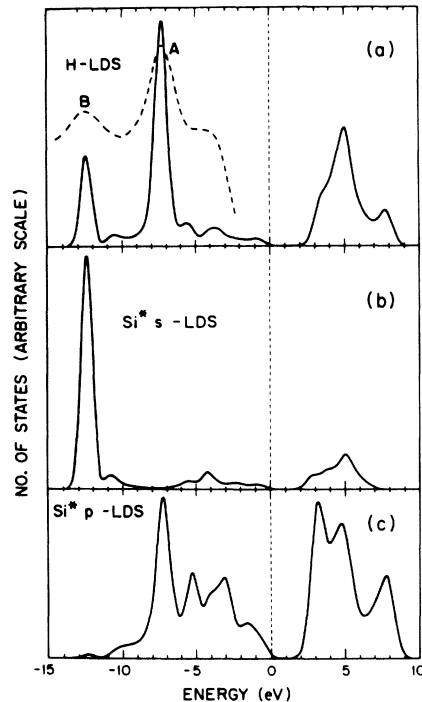

FIG. 4. The solid curves are local density of states of the valence and conduction bands of a-Si containing an SiH$_2$ unit: (a) LDS of the H atoms, (b) the 3s component of the LDS of the Si atom attached to H, (c) the 3p component of the LDS of the Si atom attached to H. The photoemission data (A-B-type) of Ref. 7 are included in (a) as a dashed curve with a shift in energy to match peak A of their data to the tall peak of the calculated H-LDS.

SiH$_2$ (5.1 eV) and SiH$_3$ (5.3 eV) are nearly equal even though the individual peaks are shifted by about 1 eV. Unlike the case of SiH, we find very little background structure for the dihydride and trihydride, especially the latter. The sharpening of peaks in going from SiH to SiH$_3$ indicates a reduction of interaction of the hydride with other Si atoms. This can be understood by comparing the local environment of the SiH$_3$ group in the CRTN with that of SiH as shown in Figs. 1(c) and 1(a). The SiH$_3$ group is relatively isolated from the rest of the CRTN and therefore behaves more like a single unit. Also the presence of three H atoms makes the Si* atom more distinctly different from the other Si atoms, thereby favoring the formation of localized states. It is also interesting to examine how the Si* p–LDS of the VB varies from SiH to SiH$_3$ [Figs. 3(c), 4(c), and 5(c)]. In the case of the monohydride, there are two major peaks of about equal height at –2.5 and –6.8 eV, the former being related to that of pure a-Si (Fig. 2), and the latter to Si 3p–H 1s bonding. For SiH$_3$, the VB Si* p–LDS consists mainly of just the Si 3p–H 1s bonding peak with only some weak struc-

tures at higher energies. This illustrates a transfer of VB energy levels to ~–8 eV from the region near the top as H atoms are introduced. This transfer occurs because the formation of the Si–H bond ties off some of the Si* 3p orbitals which would otherwise contribute to the VB levels near the top, had there been no H atoms.

For the CB the centroid of the H atoms LDS shifts to lower energy as we change from SiH to SiH$_3$. However, none of the three hydrides show gap states.

Photoemission experiments of a-Si:H were first reported by von Roedern, Ley, and Cardona.[7] For samples prepared by reactive sputtering in argon-hydrogen atmosphere, a strong peak called A and a weak peak called B at a lower energy are observed. With 50 at. % H$_2$ in the sputtering gas, the observed energies of peaks A and B are –6.3 and –11.3 eV, respectively. These may be compared with the two calculated H-LDS peaks for SiH$_2$ (at –7.3 and –12.4 eV) and for SiH$_3$ (at –8.2 and –13.5 eV). Although the observed energies of the

individual peaks differ by 1 eV or more from the calculated values, there is good agreement between our calculations and experiment as far as the energy spacing between the two peaks is concerned. Von Roedern et al. pointed out[11] that experimentally the position of the VB top is strongly dependent on the H content of the sample and is not a good reference for comparing theory with experiment. Accordingly they shifted the energy scale so as to align the strong peak of our calculated H-LDS for SiH$_3$ to their peak A.[11] In the present work we adopt a similar approach and include in Figs. 4(a) and 5(a) the experimental data of von Roedern et al. (dashed curves) with an appropriate energy shift in each case to align the highest peak. The broad shoulder at ~−4 eV in the photoemission data is associated with pure a-Si (Si $3p$) as is evident from Fig. 1 of Ref. 7, therefore, there is no counterpart in the calculated H-LDS. Excluding this shoulder from our consideration, we find a good overall resemblance between photoemission data and our calculation. Also observed by von Roedern et al. is a gradual
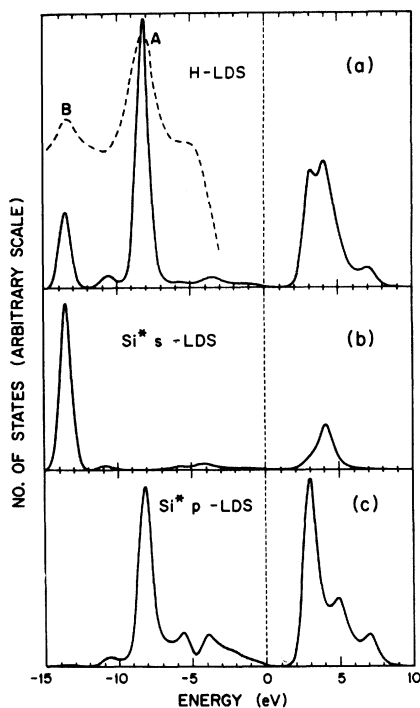

FIG. 5. The solid curves are local density of states of the valence and conduction bands of a-Si containing an SiH$_3$ unit: (a) LDS of the H atoms, (b) the $3s$ component of the LDS of the Si atom attached to H, (c) the $3p$ component of the LDS of the Si atom attached to H. The photoemission data (A-B-type) of Ref. 7 are included in (a) as a dashed curve with a shift in energy to match peak A of their data to the tall peak of the calculated H-LDS.

recession in the leading edge of the photoemission data, which is intensified with increasing H$_2$ sputter gas pressure. One can anticipate this from the theoretical results. As explained earlier in this section, insofar as the Si* orbitals are concerned, formation of hydride units in a-Si causes a transfer of energy levels from the upper edge of the VB to the region of about −8 eV. As the H concentration in the a-Si sample is increased, more Si atoms are bonded to H so that a significant fraction of the total Si atoms is of the Si* type, and the depletion of energy levels near the VB edge becomes noticeable.

In Ref. 7 were reported different photoemission spectra for samples produced by sputtering in an atmosphere containing 10 at. % H$_2$ onto a substrate held at 350 °C. The main features are two peaks, called C and D, at −5.3 and −7.5 eV which do not change with increasing amount of H$_2$ in the sputtering gas. Von Roedern et al. also found that by annealing at 400 °C samples that were prepared at room temperature, the spectra changed from the A-B type to the C-D type accompanied by evolution of H$_2$ gas.[7] In a more recent paper, von Roedern, Ley, Cardona, and Smith[11] reported a C-D-type spectrum for samples prepared by glow discharge and annealed at 350 °C, and pointed out the correspondence of their observed C-D splitting of 2.4 ± 0.2 eV with our calculated peaks at −7.0 and −10.0 for the SiH configuration. For juxtaposition we present the experimental data (dashed curves) in Fig. 3(a) with a shift in energy scale to match peak C with the central strong peak of the calculated H-LDS for SiH. Reasonable agreement is seen. It is suggested by von Roedern et al. that annealing of a-Si:H with polyhydride (SiH$_2$ and/or SIH$_3$) configurations drives out H atoms so that the resulting samples exhibit spectra[11] which may be attributed to SiH.

B. Broken-bond model

Motivated by the observation that H atoms can be incorporated into a-Si at concentrations far in excess of what is needed to tie off the dangling bonds, we propose a broken-bond (BB) model in which an Si–Si bond in an a-Si CRTN is broken and two H atoms are inserted to form an SiHHSi complex. In the absence of any clear-cut criteria for optimizing the geometry, we examine several structures with different values of the Si—H and H—H distances. We first consider three different models with the Si–H bond length fixed at 1.48 Å and the H–H distance being 0.87, 0.96, and 1.05 Å. The LDS for these three cases are plotted in Figs. 6(a)–6(c). They show a general resemblance to the curve for an isolated SiH in a-Si except for
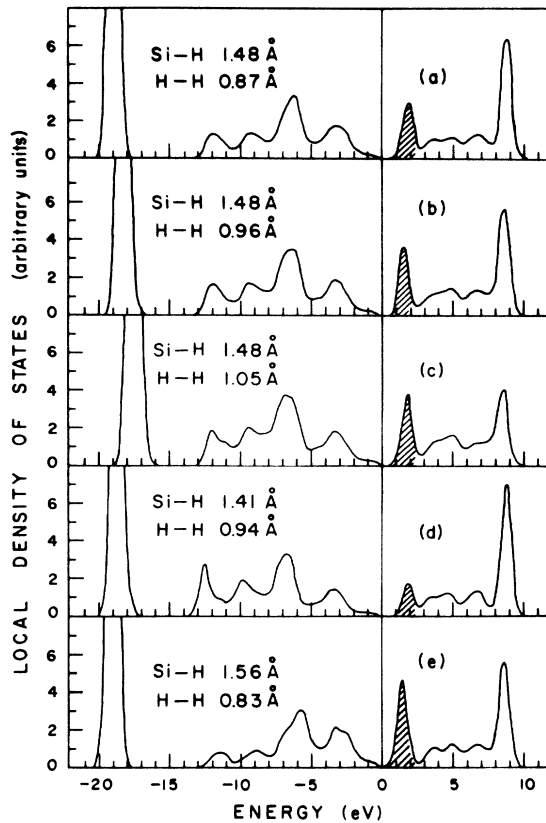
FIG. 6. Hydrogen local density of the valence and conduction bands for five broken-bond models with parameters given in the figure. The shaded areas correspond to gap states.

two additional features, i.e., the intense peak at ~−18 eV and the appearance of gap states near the CB edge (shown as shaded areas in the figure). To explain these new structures, let us consider one SiH component in the SiHHSi complex and designate its bonding and antibonding orbitals as ψ_1^b and ψ_1^a, respectively. Similarly the corresponding orbitals for the other SiH are ψ_2^b and ψ_2^a. The peak at −18 eV arises from the bonding interaction between ψ_1^b and ψ_2^b (in which the Si function is primarily s type). Likewise we attribute the gap states to those with bonding combinations of ψ_1^a and ψ_2^a. For a single SiH in a-Si, the ψ^a-type states are in the CB, but with SiHHSi the interhydride bonding pushes these states to the gap. Examination of the wave functions associated with these interhydride bonding states indeed reveals a concentration of charge between the two H atoms. For the three BB models [Figs. 6(a)–6(c)] 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 up 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 rarefraction of gap states. This is confirmed by a calculation [Fig. 6(d)] using 1.41 and 0.94 Å for the Si–H and H–H distances, respectively. Conversely, moving the H atoms away from the Si atoms causes an increase in the Si–H length and a decrease in the H–H distance. This intensifies the interhydride bonding and therefore enlarges the gap-state peak as illustrated in Fig. 6(e).

We believe that the BB model is a plausible bonding structure in a-Si:H. It can be used to explain the formation of gap states near the CB edge by hydrogenation at increasing concentrations as inferred by photoconductivity experiments.[3] This model is also consistent with the presence of two different kinds of SiH units as suggested by Freeman and Paul.[9] In this connection one may mention that Bermejo and Cardona,[29] in their study of infrared absorption of a-Ge:H, pointed out the possibility of having two single Ge–H bonds pointing toward each other. The calculated H-LDS of the VB is compatible with the observed C-D-type photoemission data. Moreover, the BB model provides a simple mechanism for incorporating H atoms to quite high concentrations.

C. $(SiH_2)_2$ model

The appearance of gap states due to interhydride bonding motivated us to study models containing SiH_2–SiH_2 configurations. Knight et $al.$ concluded from their study of the infrared and Raman spectra that the majority of the H atoms in a-Si:H appear as short $(SiH_2)_n$ chains.[6] We have examined three $(SiH_2)_2$ models with Si–Si distances covering 2.25, 2.02, and 2.48 Å, and the calculated H-LDS are shown in Figs. 7(a)–7(c). Again we find gap states near the CB edge, although they are not as conspicuous as the ones for the BB model because of the larger H–H distances across the two adjacent SiH_2 components. The VB structure in Fig. 7 is similar to that of an isolated SiH_2 except for the extra peak at the low-energy end (−14 eV) which is a manifestation of interhydride bonding, analogous to the "−18 eV peak" in Fig. 6. The interhydride bonding intensifies upon contracting the Si–Si bond from 2.25 [Fig. 6(a)] to 2.02 Å [Fig. 6(b)]. Indeed we see that the gap states are better developed, the bottom VB peak becomes more distinct, and a shoulder develops in the $Si3p$–$H1s$ peak at −7 eV. These trends are found to reverse when the Si–Si bond is lengthened (2.48 Å), as illustrated in Fig. 7(c).

The H-LDS in the VB obtained for the $(SiH_2)_2$ model as well as the existence of gap states near the CB edge are in good agreement with experiment. Also the $(SiH_2)_n$ structure is capable of
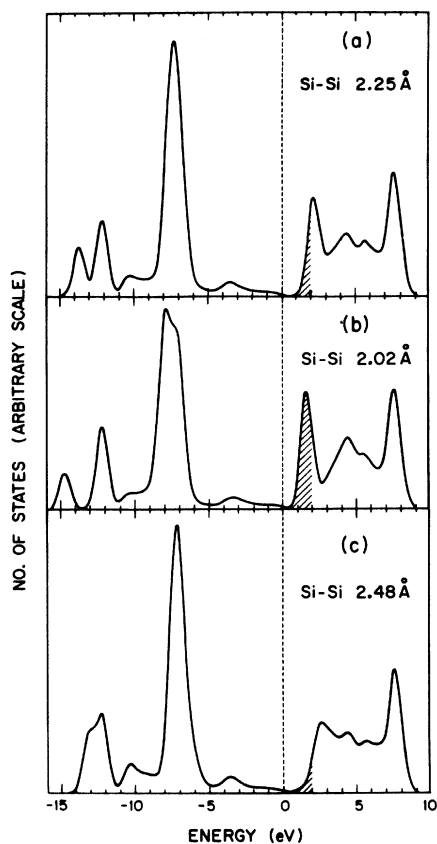
FIG. 7. Hydrogen local density of states of the valence and condition bands for three $(SiH_2)_2$ models with Si–Si distances given in the figure. The shaded areas correspond to gap states.
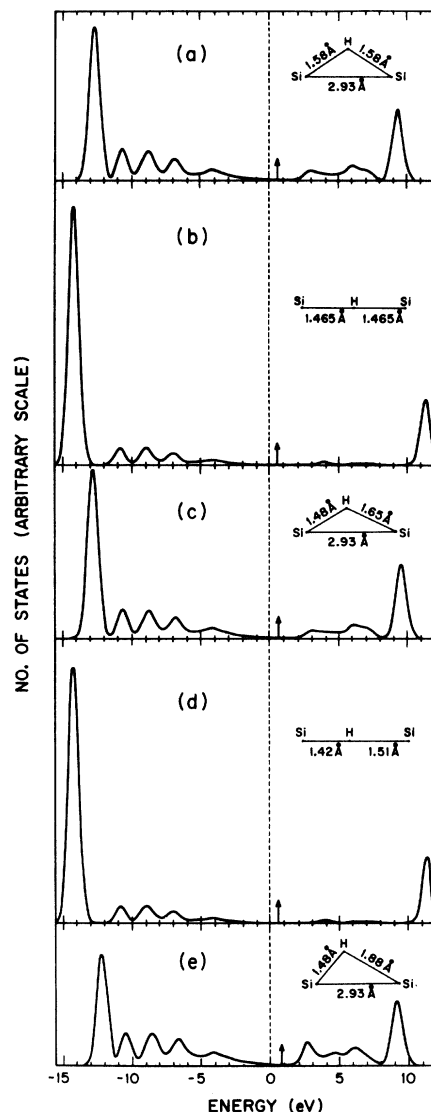

FIG. 8. Hydrogen local density of states of the valence and condition bands for five bridge models (SiHSi) with parameters shown in the figure. The arrows denote gap states.

accomodating a large number of H atoms. While we have not studied the higher polymeric form $(SiH_2)_n$, it is reasonable to expect that upon lengthening the $(SiH_2)_n$ chain, the gap states would persist and may become more abundant as a result of more interhydride interaction.

D. The SiHSi bridge model

Recently Fisch and Licciardello[30] proposed that a-Si:H contains significant numbers of SiHSi three-center bonds. McMillan and Peterson,[31] on the other hand, concluded from their kinetic analysis that if there are three-center bonds at all, their concentration must be lower than 10^{19} cm^{-3}. We have therefore examined five different configurations of the SiHSi bridge model (linear, nonlinear, symmetric, and unsymmetric, the Si–Si distance being fixed at 2.93 Å) as shown in Figs. 8(a)–8(e) along with the calculated H-LDS. In all five cases we find a strong peak at the bottom of the VB and several much weaker peaks at higher energies. The states associated with

the strong peak contains predominantly admixture of the Si* $3s$ wave functions (with very little $3p$) and therefore can be pictured as SiHSi three-center bonding orbitals formed by s-type functions from each atom. For the states at the upper VB, the Si* orbitals appear mainly as $3p$ rather than $3s$. A single gap state is found for each configuration with energy in the range of 0.63–0.84 eV above the edge of the VB, and is represented by an arrow in the LDS graphs in Fig. 8. Its wave function has almost negligible amplitude at the H atom, and the Si* orbitals involved are chiefly $3p$. This gap state indeed corresponds to the one

predicted by the authors of Ref. 30, but is quite
different from those discussed in Sec. IV B and
IV C which are due to interhydride interaction and
lie near the CB edge.

The H-LDS shown in Fig. 8 are at distinct
variance with the observed photoemission spectra.
Thus we conclude that the SiHSi bridges are not
a major constituent in a-Si:H.

E. Ring-center and interstitial models

Somewhat analogous to the bridge model, we
consider the possibility of placing an H atom at
the center of a six-member ring in the RPB
CRTN of a-Si (ring-center model). The H-LDS
[Fig. 9(a)] again has an intense peak at the bottom
of the VB and several smaller ones at increasing
energy toward the top of the VB. This VB part of
the curve bears some resemblance to that of the
SiHSi bridge model, but we find no gap states
here. We also consider a model with an interstit-
ial H atom surrounded by four Si atoms with
nearly the same distance (interstitial model). In
both the ring-center and the interstitial model,
the tetrahedral connectivity of the a-Si network
is not destroyed. The H-LDS for the interstitial
model, shown in Fig.9(b), has two strong peaks
in the upper part of the VB (−1.2 and −5.3 eV)
and a much weaker one at the bottom (−12.5 eV).
The Si* orbitals involved in the −1.2- and −5.3-
eV group are more predominantly $3p$, whereas the
Si* admixture for the states at −12.5 eV is chiefly
$3s$. Clearly we can rule out the ring-center model
as an important contender. As to the intersitital
model, the discrepancy between the H-LDS and
experiment is not as striking, yet the lack of
quantitative agreement in the spacing of the peaks
leaves it much less acceptable than the hydride,
BB, and $(SiH_2)_2$ models.

V. DISCUSSION AND CONCLUDING REMARKS

In this paper we present first-principles calcu-
lations of the electronic energy of a-Si:H based
on a series of different structural models, and
use the results, in conjunction with experiments,
as a step toward identifying the important H-
bonding configurations. Since this is, to our know-
ledge, the first published report on first-princi-
ples electronic-energy calculations[32] for a-Si:H,
it is instructive to give an overview of the state of
the art especially in reference to similar calcula-
tions for crystalline solids. Following this we will
discuss the various structural models in the light
of our theoretical study.

The input to our electronic-energy calculation is
a structural model for the atomic positions in the
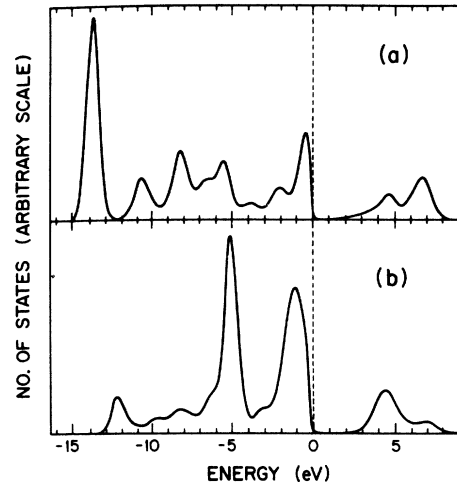solid. The CRTN models constructed by computer

FIG. 9. Hydrogen local density of states of the valence
and condition bands for (a) the ring-center model, (b)
the interstitial model.

relaxation in accordance with certain potential
functions prove to be successful for intrinsic a-Si;
we have used them as the input for calculating the
dielectric function of intrinsic a-Si and the results
are in good agreement with experiment.[15] Our
a-Si:H structural models used here are construc-
ted in a similar manner. Once the positions of the
atoms in a-Si:H are given, the calculation of
electronic energies parallels closely to that for
crystalline solids with point defects.[24] The major
difference is that because of the much greater
structural complexity, the one-electron Hamil-
tonian for a-Si:H is generated by a superposition
of atomic potentials rather than by a self-consis-
tent-field (SCF) iteration procedure as is often
done for crystals. As indicated in Sec. III, we
had used a similar superposition of these same
individual potentials to calculate the ionization
energies of the valence levels of SiH_4 as a check,
and the results agree well with experiment. Al-
though we are not able to perform an SCF calcula-
tion for a-Si:H, we nevertheless attempted to get
some idea of its effects on our results. To this
end we did several test calculations for the BB
model by varying in five different ways the poten-
tial in the vicinity of the SiHHSi complex so as to
simulate qualitatively the kind of change that may
be produced by an SCF iteration. Aside from
slight shifts of the peak structures, the key fea-
tures of the calculated H-LDS remain the same
in all cases.

In order to keep the computation tractable, we
limit ourselves to the cases of a single "defect"
configuration. These results should be applicable
also to samples containing several different kinds
of configurations if they appear at low concentra-

tions. However, it is not uncommon to have H concentrations as high as 30 at. %, hence questions may arise as to possible interactions between different units. This can be assessed by making comparison between SiH_2 and $(SiH_2)_2$, and between SiH and SiHHSi. In both cases the VB H-LDS of the "dimers" [$(SiH_2)_2$ and SiHHSi] and "monomers" (SiH_2 and SiH) are alike except for some additional features in the "dimers" due to the interaction of the two components. In an a-Si:H network it is extremely unlikely to have two units closer than the two SiH components in SiHHSi. Thus, even for samples at moderatly high concentrations of H, the interactions among the H-bonding units are not expected to greatly alter the VB results of our calculations except for modifications which do not change the gross features. On the other hand, these interactions may have stronger effects on the CB where the states are more extended, but at this stage we are not so much concerned with the CB states.

The CRTN modeling of atomic positions in a-Si:H is, of course, not a unique process. A particular H-bonding configuration may be found in different local environments throughout the amorphous sample. It is, therefore, more realistic to represent a-Si:H as an ensemble of many different CRTN rather than a single one. To address this point, we have independently built two models for the SiH configuration. The two sets of calculated H-LDS have similar multiple-peak structure with only small difference in the peak position. Compared to the monohydride, the SiH_2 and SiH_3 configurations have simpler VB H-LDS structure, i.e., only two peaks with one corresponding to Si $3p$–H bonding and the other to Si $3s$–H. Thus we expect to find this double-peak feature in different CRTN models of SiH_2 and SiH_3, even though we have not performed test calculations. Furthermore, since the separation between these two peaks is nearly the same for our SiH_2 and SiH_3 models (5.1 and 5.3 eV), we believe that this peak spacing should be insensitive to local environment. For the cases of the BB and $(SiH_2)_2$ models, the two new features are the gap states and the peak below or near the bottom of the VB. Both arise from interhydride bonding rather than interactions involving the Si atoms around the individual complex. Hence the general features of our calculated H-LDS are expected to persist upon an ensemble average of various CRTN models.

Among the models considered in this paper, we recognize two distinct patterns in which the H atoms are attached to Si. In the hydride, BB, and $(SiH_2)_2$ models, each H atom is chemically bonded to a Si atom by sharing a pair of electrons,

whereas the bridge, ring-center, and interstitial models place an H atom in the vicinity of two or more Si atoms with the result of unpaired electrons. The models in the first category are all consistent with photoemission experiments. Specifically a-Si:H prepared by reactive sputtering in Ar–H_2 at room temperature exhibits photoemission spectra similar to the VB H-LDS of SiH_2, SiH_3, and $(SiH_2)_2$, but for samples prepared by holding the substrate temperature at 350 °C, one finds in the observed spectra characteristics of SiH and SiHHSi.[7,11] With only photoemission spectra pertaining to the VB, one cannot distinguish between SiH and SiHHSi, or between SiH_2 and $(SiH_2)_2$, since their differences are most noticeable either below the VB or in the upper gap region. However, in view of the inferred gap states as suggested by photoconductivity experiments,[12] it is likely that both SiH and SiHHSi are present in samples which exhibit monohydride characters, and both SiH_2 and $(SiH_2)_2$ [or $(SiH_2)_n$] in samples with dihydride-type spectra. It is also reasonable to believe that all SiH, SiH_2, SiH_3, SiHHSi, and $(SiH_2)_n$ may be present with their relative abundance varying from one kind of sample to another. It would be desirable to extend the photoemission experiment to the energy region near and below the bottom of the VB to study the interhydride bonding peak. As to the models in the second category (bridge, ring-center, and interstitial), our analyses in the preceding section indicate that they do not qualify as major constituents in a-Si:H. Nevertheless, it is interesting to note the large change in H-LDS from the ring-center model to the interstitial model. Also the disagreement with the experimental photoemission data is much smaller for the interstitial model. It may even be possible to further reduce this discrepancy by putting the H atoms at some other locations. However, we have not pursued this line of investigation.

In summary the immediate conclusions that we can make from this study are as follows:

(i) Of the models that had been proposed previously for H-bonding configurations in a-Si:H, the isolated-hydride and $(SiH_2)_2$ models are consistent with the observed photoemission spectra.

(ii) We propose a BB model, SiHHSi, which is found to be consistent with the photoemission experiment and the suggestion of two kinds of SiH units.[9]

(iii) Due to interhydride bonding, the BB and $(SiH_2)_2$ models give gap states near the CB edge which is in accordance with the results of photoconductivity experiment,[12] but no gap states are found for the isolated hydrides.

(iv) The SiHSi bridge model, ring-center mo-

del, and interstitial model give VB H-LDS which are at variance with the photoemission spectra, and therefore are not appropriate for the major constituents in a-Si:H.

It is gratifying that first-principles calculations of electronic energies for amorphous solids have advanced to the stage that they can be used, with a reasonable degree of confidence, to analyze experimental data and derive from them structural and other information. The same kind of theoretical approach should be fruitful for studying such topics as effect of doping, various defect structure,[33] and incorporation of F or Cl atoms (in place of H) in a-Si.

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