

## Theoretical models for the electronic structures of hydrogenated amorphous silicon

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Self-consistent-field  $X\alpha$  scattered-wave molecular-orbital calculations have been carried out for silane molecules and clusters which are models for local atomic configurations in hydrogenated amorphous silicon. The results are in good agreement with measured photoelectron and optical spectra and provide insight into the electrical transport properties of this material.

There has been a resurgence of interest in the electronic and transport properties of amorphous silicon ( $\alpha$ -Si) following the discovery that this material, when hydrogenated to saturate dangling bonds coordinately, can be substitutionally doped, which has enabled the fabrication of solar cells based on  $\alpha$ -Si.<sup>1</sup> In this article we present theoretical models for the electronic structures of hydrogenated  $\alpha$ -Si, which can be used as a basis for understanding the optical and electronic properties of this material, including recently measured photoelectron spectra.<sup>2</sup> The theoretical models are constructed from first-principles molecular-orbital calculations for representative molecules and clusters using the self-consistent-field  $X$ -alpha scattered-wave (SCF- $X\alpha$ -SW) method.<sup>3</sup> This technique has been applied extensively to polyatomic molecules and solids,<sup>4</sup> including covalently bonded systems such as diamond and vacancies therein,<sup>5</sup> crystalline silicon,<sup>6</sup> silicon surfaces,<sup>7</sup> and impurities in silicon.<sup>6,8</sup> The appropriate values for the exchange-correlation parameters  $\alpha$  for the component atoms are  $\alpha_{\text{Si}} = 0.72751$  and  $\alpha_{\text{H}} = 0.7772$ .<sup>3</sup>

To calibrate the theoretical description of silicon-hydrogen bonding and to model polysilanelike (dihydride) configurations characteristic of hydrogenated  $\alpha$ -Si deposited at low substrate temperatures, we have first carried out SCF- $X\alpha$ -SW calculations for the structurally and spectroscopically well-characterized  $n$ -silane molecules<sup>9</sup>  $\text{Si}_n\text{H}_{2n+2}$  ( $n = 2, 3, \dots, 6$ ), with the bond distances  $d(\text{Si-Si}) = 2.35$  Å and  $d(\text{Si-H}) = 1.48$  Å and tetrahedral bond angle ( $109.47^\circ$ ). For  $n = 4-6$ , we have considered only the linear conformational isomers. The resulting  $n$ -silane molecular-orbital energy levels are shown in Fig. 1 along with the corresponding SCF- $X\alpha$  energy levels calculated for the free Si and H atoms. Also shown, for comparison, are the calculated levels for the coordinately unsaturated disilene molecule  $\text{Si}_2\text{H}_4$ . To clarify discussion, the

molecular energies have been shifted so the average energy of region II for each molecule matches the H-1s atomic energy.<sup>10</sup> The blocks separating the atomic energies and molecular-energy groupings indicate the energy span for the three main regions (I, II, and III) of occupied valence states and region IV of unoccupied states for hexasilane  $\text{Si}_6\text{H}_{14}$ . The dark regions indicate the variation in the contribution of H(1s)-like charge density to the molecular-orbital charge distributions throughout each region. The energy gap separating the highest occupied valence orbital from the lowest unoccupied orbital decreases from 5 eV for  $\text{Si}_2\text{H}_6$  to 3.5 eV for  $\text{Si}_6\text{H}_{14}$ , in good agreement with the observed decrease in the threshold energy for optical absorption with increasing silicon chain length.<sup>11</sup>

The primary and secondary correlations between atomic and molecular orbitals are indicated by the solid and dashed connecting lines, respectively, in Fig. 1. Briefly, the molecular orbitals of region I correspond to Si(3s)-H(1s) bonding orbitals, those of II to H(1s)-Si(3p) bonding orbitals, and those of III to Si(3p)-Si(3p) bonding orbitals with secondary H(1s) bonding contributions. Contour maps of typical molecular orbitals in these three regions are shown in Fig. 2 for the disilane molecule  $\text{Si}_2\text{H}_6$ . There is negligible Si  $s$ - $p$  hybridization in the orbitals of region III;  $s$ - $p$  hybridization in regions I and II is small and roughly parallels the variation in H(1s) character therein. Si(3s)-Si(3s) and Si(3p)-Si(3p) antibonding orbitals are responsible for the unoccupied levels constituting region IV, although spatially delocalized, Si(3d)-like orbitals and antibonding H(1s)-like orbitals also contribute significantly to the upper states of this manifold.

One can compare the calculated  $n$ -silane electronic structures with photoelectron spectra<sup>9</sup> measured for  $n = 2, 3, 4$ , and 5. On the right-hand side of Fig. 1, we compare the experimental photoelectron spectrum of pentasilane ( $\text{Si}_5\text{H}_{12}$ ) with the theo-

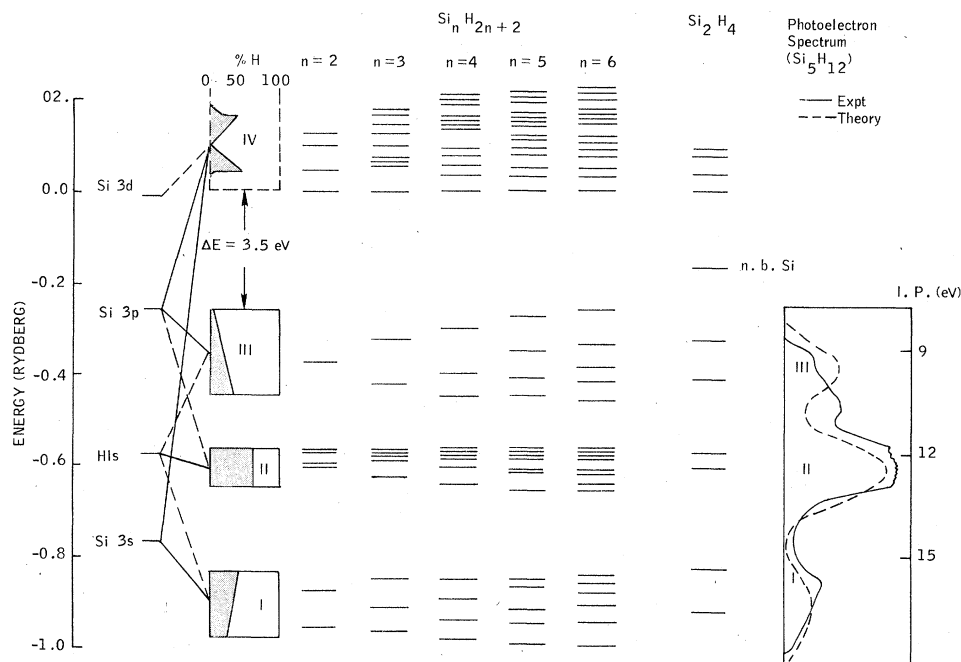


FIG. 1. SCF- $X\alpha$  orbital energy levels of  $n$ -silane molecules; including comparison of experimental and theoretical photoelectron spectra for the  $\text{Si}_5\text{H}_{12}$  molecule.

retical spectrum derived from SCF- $X\alpha$ -SW transition-state calculations<sup>3</sup> of the ionization potentials, which include the effects of orbital relaxation, in conjunction with the computational procedure developed by Davenport<sup>12</sup> for evaluating photoelectron cross sections directly from SCF- $X\alpha$ -SW orbital wave functions. The two spectra are in generally good agreement. The H(1s)-Si(3p) bonding orbitals of region II are responsible for the high-intensity "central" peak, whereas the Si(3s)-H(1s) and Si(3p)-Si(3p) bonding orbitals of regions I and III, respectively, are responsible for the other two main peaks. Using semiempirical complete-neglect-of-differential overlap (CNDO) calculations, Bock *et al.*<sup>9</sup> concluded that region III of their pentasilane spectrum could only be fit by considering the coexistence of several rotomers. The discrepancies in this region between the present computations and the experimental spectrum might be attributable to the neglect of the other rotomers. The photoelectron spectra<sup>9</sup> measured for other  $n$  silanes ( $n=2, 3$ , and 4) can be interpreted in a similar way.

If one views the  $n$ -silanes as discrete molecular analog of polysilane like  $(\text{SiH}_2)_n$  dihydride configurations in amorphous hydrogenated silicon deposited at low substrate temperature,<sup>13</sup> then the "A" and "B" peaks in the photoelectron spectrum of such material measured by von Roedern *et al.*<sup>2</sup>

can be interpreted as corresponding to the hydrogen-induced regions II and I, respectively, of such configurations. On the other hand, the latter authors have argued that peaks A and B are due to trihydride ( $\text{SiH}_3$ ) configurations. We discuss this issue in a later section in terms of a theoretical model for the electronic structure of  $a$ -Si containing trihydride groups.

Along with the  $n$ -silane electronic structures summarized in Fig. 1, we have also carried out SCF- $X\alpha$ -SW molecular-orbital calculations for the coordinately unsaturated molecule disilene ( $\text{Si}_2\text{H}_4$ ), keeping, however, the Si-Si bond distance and H-Si-H tetrahedral bond angle characteristic of disilane ( $\text{Si}_2\text{H}_6$ ).<sup>14</sup> The main groups I, II, III, and IV of orbitals characteristic of  $n$ -silane are also present in disilene, although there is an empty nonbonding Si(3p)-Si(3p) orbital split off in energy from the top of the valence manifold III and effectively located within the band gap separating regions III and IV of the  $n$ -silanes. In the spirit of using the  $n$ -silanes as models for coordinately saturated polysilanelike configurations in hydrogenated  $a$ -Si, we can view disilene ( $\text{Si}_2\text{H}_4$ ) as a simple molecular analog of coordinately unsaturated neighboring Si sites in this material, with the unoccupied silicon nonbonding spin orbital having the significance of a degenerate pair of empty states within the band gap. The addition of

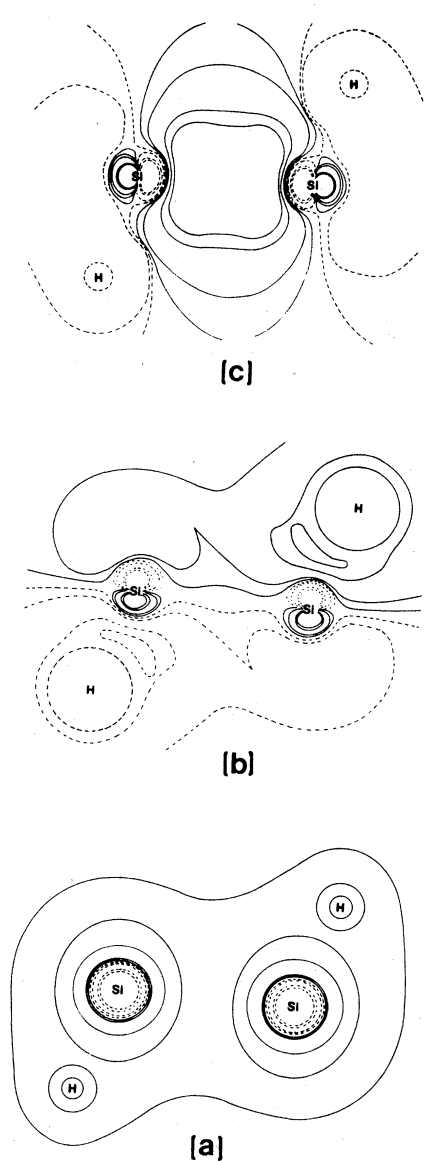


FIG. 2. Contour maps, plotted in the plane of the Si-Si bond and two Si-H bonds, of the principal (a) Si(3s)-H(1s), (b) H(1s)-Si(3p), and (c) Si(3p)-Si(3p) bonding orbitals for the  $\text{Si}_2\text{H}_6$  molecules corresponding to the energy levels in regions I, II, and III, respectively, of Fig. 1.

an H atom to one of the two Si sites will create a Si-H bonding orbital within the valence-band manifold and a half-occupied nonbonding orbital within the band gap leading to a net local spin density. However, we have not considered symmetrical three-center bonding configurations of the type recently discussed by Fisch and Licciardello,<sup>15</sup> nor have we investigated the range of possible de-

fect states in amorphous silicon recently described by Adler.<sup>16</sup> Chin *et al.*<sup>17</sup> have recently presented calculations of the density of new states produced by the introduction and interactions of two adjacent monohydride groups, an additional possible defect configuration not considered by Adler.<sup>16</sup>

One can construct a theoretical model for the local electronic structure of pure  $\alpha$ -Si based on the 17-atom cluster  $\text{Si}_5(\text{sat})_{12}$ , where the central Si atom is tetrahedrally coordinated by four nearest-neighbor Si atoms, each of which is coordinatively saturated by three hydrogen atoms at a Si-H distance equal to the normal Si-Si distance. Such a cluster has previously been used by Cartling<sup>6</sup> and Hemstreet<sup>8</sup> in SCF- $X\alpha$ -SW studies of crystalline silicon and of localized impurity states in crystalline silicon. The resulting cluster molecular-energy levels are shown on the left of Fig. 3, and their correspondence to the valance and conduction bands of pure  $\alpha$ -Si is indicated. For comparison of the  $\text{Si}_5(\text{sat})_{12}$  electronic structure with available photoemission<sup>18</sup> and optical spectra of amorphous Si, an "optical density of states" was determined by a Gaussian broadening of the energy levels, weighting the occupied "valence" levels in proportion to photoionization cross section evaluated by Davenport's<sup>12</sup> procedure and weighting the unoccupied "conduction" levels in proportion to their contributions to optical oscillator strengths evaluated by Noodleman's<sup>19</sup> procedure. The onset of orbitally allowed, optically-induced electronic excitations in the  $\text{Si}_5(\text{sat})_{12}$  cluster, determined by the transition-state procedure,<sup>3</sup> is 1.3 eV, which agrees with the optically measured<sup>20</sup> energy gap of 1.26 eV in pure amorphous silicon sputtered at 25 °C, although gaps as high as 1.6 eV have been reported<sup>21</sup> for  $\alpha$ -Si deposited by silane pyrolysis at 550 °C.

An analogous model for the high-temperature "monohydride" form of hydrogenated  $\alpha$ -Si is a  $\text{Si}_4\text{H}(\text{sat})_9$  cluster, in which a single hydrogen atom is substituted for one of the silicon atoms in the tetrahedrally coordinated  $\text{Si}_5(\text{sat})_{12}$  corresponding to a Si-H alloy containing 16 at. % H by counting each saturator as 0.25 Si atoms. The calculated energy levels are shown in the center of Fig. 3 along with the corresponding optical density of states. The principal hydride levels are labeled according to the percentage of hydrogen in the cluster molecular orbital. The main difference between the electronic structures of the  $\text{Si}_5(\text{sat})_{12}$  and  $\text{Si}_4\text{H}(\text{sat})_9$  clusters is the occurrence of silicon-mohydride bonding orbitals embedded in the valence manifold well below the band edge, leading to the hydrogen-induced peaks C and D in the density of states. The effective band gap is increased to 1.7 eV. Only a small amount of Si-H

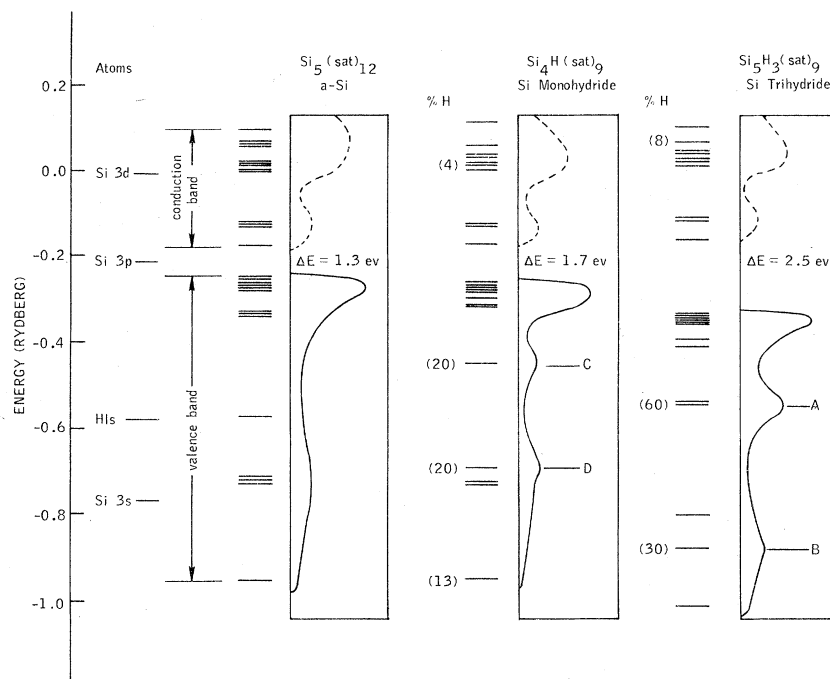


FIG. 3. SCF- $X\alpha$  molecular-orbital energy levels and "optical densities of states" of coordinatively saturated clusters representing pure  $\alpha$ -Si, Si monohydride, and Si trihydride.

antibonding character is present in the conduction manifold, well above the conduction-band minimum. The results are consistent with the occurrence of two hydrogen-induced peaks *C* and *D* in the photoemission spectrum of  $\alpha$ -SiH and with the optically measured band gap of 1.6 eV in typical  $\alpha$ -SiH<sub>x</sub> alloys containing about 20% H bonded as monohydride.<sup>22</sup> In addition to the *C* and *D* peaks, the photoemission spectrum of the monohydrated silicon taken with He II excitation reveals a third peak at 10.5 eV below  $E_F$ . This peak, which is not discussed by the authors, appears to correspond to the lowest valence-band molecular orbital shown for the monohydride cluster in Fig. 3.

Finally, SCF- $X\alpha$ -SW molecular-orbital calculations have been carried out for a Si<sub>5</sub>H<sub>3</sub>(sat)<sub>9</sub> cluster (three H atoms tetrahedrally coordinated to a single Si site) corresponding to a Si-H alloy containing 29.3 at. % H. This cluster provides a molecular analog to alloys containing H bonded predominantly in trihydride configurations which have been considered to exist in hydrogenated amorphous silicon deposited at 25 °C.<sup>2</sup> The results shown at the right of Fig. 3 reveal the presence of two hydrogen-induced peaks *A* and *B*, in the local density of states and a further increase of the effective band gap. The *A* and *B* levels of the cluster with a trihydride group contain significantly more hydrogen contribution than the *C* and *D* le-

vels of the cluster with a monohydride group and they have a close correspondence to the Si(3s)-H(1s) (region I) and Si(3p)-H(1s) (region II) bonding states of the "dihydridelike" polysilanes shown in Fig. 1. Thus, while the region-I and region-II states of the  $n$ -silanes for large  $n$  have been shown to provide an interpretation in terms of dihydride configurations of the photoemission spectrum<sup>2</sup> of hydrogenated amorphous silicon deposited at 25 °C, the *A* and *B* levels of the trihydride can also be correlated with this spectrum. Thus, it is difficult to distinguish spectroscopically between the dihydride and trihydride configurations on the basis of the published photoemission data.<sup>2</sup>

These theoretical studies appear to be helpful in understanding the optical and electron spectroscopy of two families of materials, the poly  $n$ -silane molecules and the hydrogenated amorphous silicon alloys, and in establishing chemical trends within and between these two families of materials. The original motivation for initiating these studies was to better understand the relationship between electronic structure and the photovoltaic response of the hydrogenated silicon amorphous alloys. We have shown a significant trend of increasing band gap with increasing hydrogen content from 1.3 eV for pure Si to 1.7 eV for 16% H bonded as monohydride to 2.5 eV for 29.3% H bonded as trihydride.

With regard to the question of hydrogen character in the electronic states near the band edges we have found much more hydrogen character concentrated near the top of the valence band than near the bottom of the conduction band in contrast to expectations<sup>23</sup> based on a comparison of photoemission results for H on the (111) surfaces of Si and the calculated bonding to antibonding transition in SiH<sub>4</sub>. Thus the change of band gap with hydrogen content appears to be more affected by the hydrogen-induced hybridization of the Si(3*p*)-Si(3*p*) bonding levels at the top of the valence band than by any hydrogen-induced hybridization of the Si-Si antibonding levels at the bottom of the conduction band or by the presence of H-Si antibonding levels within the conduction band. The enhanced H character at the top of the valence band compared to the bottom of the conduction band may also be the origin of the much lower drift mobility of holes<sup>24</sup> than electrons<sup>25</sup> in this material. The finite concentration of hydrogen character at both band

edges, in addition to the progressive increase in band gap with H content, appears to indicate that the optimum photovoltaic materials will occur at a relatively low hydrogen content, in agreement with results to date. Finally, we have shown that it is possible to model defect configurations with these theoretical techniques, as exemplified by the results for disilene with its empty nonbonding orbital creating an unoccupied level in the middle of the forbidden gap of coordinatively saturated hydrogenated silicon. These techniques appear to have the potential for describing the role of bond-angle perturbations, multiple-element alloy systems, and other intriguing questions of electronic structure which cannot easily be addressed directly by experiment, and we intend to pursue these opportunities in the future.

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