Conformational effects in organopolysilanes: A first-principles approach

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A first-principles study of the electronic structure of organopolysilanes with use of a linear combination of atomic orbitals local-density-functional approach for the one-dimensional band structure is reported. Model systems were chosen to study the effects of changes of backbone conformation and alkyl substitution on the electronic structure and associated optical properties of these materials. The results are largely supportive of previous empirical and semiempirical results and find the polysilanes to be direct-gap materials with the highest occupied and lowest unoccupied states primarily silicon backbone bonding and antibonding states, respectively. We find that the band gap increases by roughly 2 eV as the backbone is twisted from the all-trans conformation to an all-gauche conformation.

INTRODUCTION

Organopolysilanes are linear high polymers composed of a chain of silicon atoms σ bonded together, with two organic substituents attached to each backbone silicon.[1] Major progress over the past decade in the synthesis and characterization of these materials has led to an increased recognition of their potential technological applications as silicon carbide precursors, as photoresists in photolithography,[2] and as photoconductors.[3] Most of these technological applications depend intimately on the electronic structure and resulting optical properties of these materials. The organopolysilanes absorb in the ultraviolet with the wavelength of maximum absorption, λ_{max}, in the range 300–400 nm (roughly 3–4 eV). Photoexcitation can cause both silicon-backbone chain scission[2,4–6] and the creation of highly mobile excitons followed by photoconduction via hole transport (after electron withdrawal).[3,5,7]

The electronic properties are strongly dependent on backbone conformation, substituents, and degree of polymerization. The absorption threshold and λ_{max} are observed to decrease in energy with increasing chain size[5] as well as with increasing substituent size.[2] Several symmetrically substituted dialkyl-polysilanes, in particular poly-di-n-hexylsilane (PDHS), have been reported to exhibit a red shift of the absorption peak of up to 60 nm with decreasing temperature and a concomitant narrowing of the line shape.[8–16] This spectral shift has been attributed to an order-disorder transition from a disordered system with a mix of trans and gauche conformers along the silicon backbone to a highly ordered system. Experimental evidence suggests an all-trans (or planar zigzag) conformation for PDHS (Refs. 13 and 14) with a shift in λ_{max} from 310–320 nm to roughly 355 nm in solution and 374 nm in solid films (corresponding to an energy shift roughly from 4.0 to 3.3–3.5 eV). Poly-di-n-pentylsilane (PDPS) exhibits a similar transition in solution,[9] but in solid films[15,16] apparently makes a transition to an ordered 7/3 helical conformation with λ_{max} of 313 nm (4.0

eV), a blue shift of 0.6 eV compared to the λ_{max} of PDHS.

The electronic states immediately about the Fermi level (i.e., the high valence-band and low conduction-band states) are believed to be highly delocalized σ-bonding and antibonding states primarily composed of silicon-backbone states. One of the major areas of theoretical study needed to understand the optical properties of the organopolysilanes is the nature of these frontier electron states, e.g., how their energies and compositions depend on conformation and substituent. A variety of theoretical methods[17–26] have been used to investigate the electronic structure of both polymeric chain systems and model molecular species. Theoretical studies of the polymeric chains have consisted primarily of semiempirical calculations of the one-dimensional band structures and the effects of substituents and conformation on the band structure.[19–21] The only published first-principles calculations heretofore have been *ab initio* calculations[18] of the electronic structure and minimum-energy geometry of the all-trans conformation of the unsubstituted polysilane chain (i.e., hydrogen atoms attached to each silicon atom).

The work presented herein describes a first-principles study of the electronic structure of the organopolysilanes using a linear combination of atomic orbitals local-density-functional (LCAO-LDF) method for calculating the one-dimensional band structures of chain polymers. Morphologically, the polysilanes are chain polymers with minimal cross linking between chains and are well suited for study with a model assuming one-dimensional periodicity. As an initial step in a broader study of these materials, one-dimensional band structures have been calculated and interpreted for a set of model polysilane chain systems that illustrate some of the basic physics and chemistry occurring in the organopolysilanes. The model systems used were chosen to study the effects of conformational changes of the silicon backbone on the electronic structure and associated optical properties of these materials. A preliminary report of this work has been presented elsewhere.[27] Our results are generally suppor-

tive of current interpretations of the nature of the low-energy excitation process and frontier states about the Fermi level in these materials. In particular, these first-principles results predict that the highest occupied and lowest unoccupied states are primarily silicon-backbone bonding and antibonding states, respectively, with the band gap increasing as the backbone is twisted from the all-trans conformation to the 7/3 helical conformation and further to the 4/1 helical conformation. This behavior appears well described by a tight-binding model using two sp^3 hybrids per silicon atom to describe the valence and conduction bands in the vicinity of the Fermi level.

APPROACH

The LCAO-LDF method used in this work has been used successfully for describing the electronic structure of π-conjugated polymers and is described in detail elsewhere.[28] This method calculates both the band structure and the total energy within the Gáspár-Kohn-Sham local-density-functional scheme[29] for a polymer chain possessing translational periodicity in one dimension. An equilibrium geometry could thus be obtained by a search for the minimum-energy conformation, although this work focuses on a study of the comparative electronic structures of a given set of model structures. The one-electron wave functions are approximated with a linear combination of nuclear-centered Gaussian basis functions. Absorption and photoelectron spectra can be subsequently estimated from interband-transition cross sections and photoionization cross sections directly calculated from the one-electron wave functions and energy levels.[28] Because the current computational implementation of the LCAO-LDF scheme requires translational symmetry, calculations were restricted to helical conformations with moderate-size translational unit cells. For example, the 7/3 helical conformations of the polysilane required calculations using a unit-cell basis containing seven silicon nuclei.

Model structures were examined in this work for the effects of both conformation and substituents. Conformational effects were studied primarily by calculation and comparison of electronic structures for three helical forms of unsubstituted polysilane (PS): an all-trans form with all silicon-backbone dihedral angles in a trans conformation, a 7/3 helical form with the silicon-backbone dihedral angles offset from the trans conformation by approximately 30°, and a 4/1 helical form corresponding to an all-gauche conformation of the silicon backbone. A depiction of these three conformations and the corresponding backbone dihedral angles is given in Fig. 1. Because of the requirement of translational periodicity and our choice of silicon backbones the resulting silicon-backbone dihedral angles differ slightly from the values that would be valid for tetrahedral bond angles—the dihedral angles actually used were roughly 148.8° for the 7/3 helix (compared to 148.4° for tetrahedral bond angles) and 62.7° (compared to exactly 60°) for the 4/1 helix. Similar calculations were performed for the all-trans and 4/1 helical conformations of the alkyl-substituted species polydimethylsilane (PDMS), in which

the methyl units ($-CH_3$) are substituted for the hydrogens attached to the backbone, to examine the effects of alkyl substituents on the electronic structure and optical properties.

For the model structures described above, appropriate bond lengths and bond angles were chosen from *ab initio* Hartree-Fock geometry optimizations for tetrasilane (Si_4H_{10}) and other model molecular species.[24] The bond lengths used were 2.35 Å for the Si—Si bonds, 1.48 Å for the Si—H bonds, 1.89 Å for the Si—C bonds, 1.54 Å for the C—C bonds, and 1.08 Å for the C—H bonds. The Si—Si—Si bond angle was chosen to be 111.7°, the same as that obtained in the earlier geometry optimization of tetrasilane.[24] For consistency with the tetrasilane results, the H—Si—H bond angle was chosen to be 108°, and the C—Si—C bond angle was also set to this value. All bond angles centered on the carbon nuclei were set to tetrahedral bond angles of 109.47°, with the hydrogen atoms staggered relative to the bonds on the nearest silicon atom. All calculations described below were calculated with a minimal basis set—$6s4p$ for silicon,[30] $4s2p$ for carbon,[31] and $2s$ for hydrogen[31]—unless otherwise
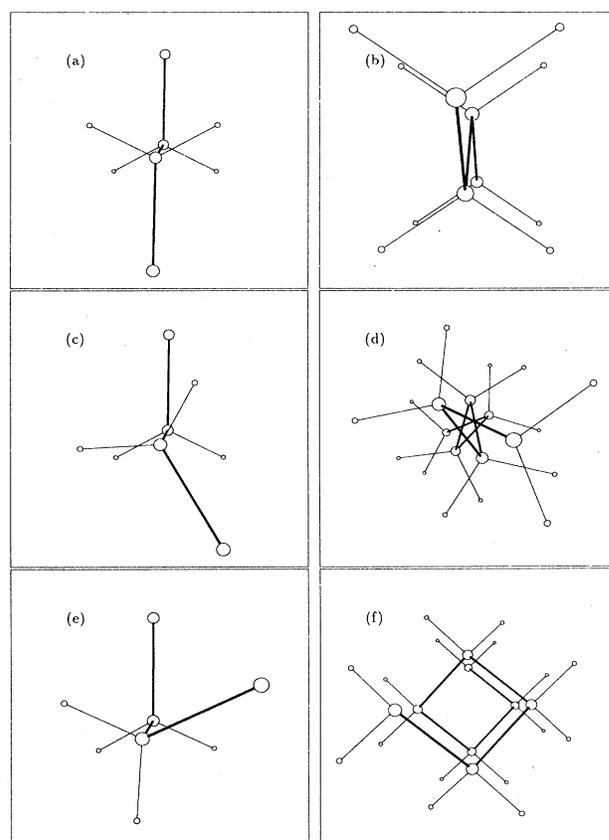
FIG. 1. Depiction of silicon-backbone dihedral angles of (a) 180°, (c) ~150°, and (e) ~60°, with the corresponding views down the chain axis of the (b) all-trans, (d) 7/3 helical, and (f) 4/1 helical conformations of polysilane. Large circles depict silicon atoms and small circles depict hydrogen atoms.

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noted. For all structures, except the 7/3 helical conformation of polysilane and the 4/1 helical conformation of polydimethylsilane, additional calculations were performed using a slightly more complete, moderate-size basis set: $10s\,6p\,1d$ for silicon,[32] $7s\,3p$ for carbon,[32] and $3s$ for hydrogen.[31]

RESULTS

Figure 2 depicts the calculated band structures for the all-trans, 7/3 helical, and 4/1 helical conformations of unsubstituted polysilane. The screw symmetry of these conformations has been used to reduce the translational unit cell to a unit cell (defined using the screw-symmetry operations) containing one SiH_2 group, and the Brillouin zone appropriately unfolded. Because the reflection plane containing the silicon nuclei in the all-trans conformation commutes with the operations of the one-dimensional translation group (and the screw-symmetry group), all one-electron wave functions will be either symmetric (σ-like) or antisymmetric (π-like) with respect to this symmetry operation, and these states are depicted appropriately in Fig. 2(a). Note that the all-trans conformations can also be generated with a glide operation instead of a screw operation, in which case the π bands would unfold differently, leading to a right-left reflection of the π band in Fig. 2(a) (as reported in earlier preliminary work[27]). In addition to this symmetry plane for the all-trans conformations, a C_2 rotation axis (perpendicular to the helical-chain axis and intersecting the silicon-nucleus position) will be present in all helical conformations. This operation does not commute with the screw-symmetry group, and thus the one-electron wave functions need only belong to the irreducible representations of the C_2 group at the high-symmetry points at the Brillouin-zone center and edge.

In agreement with earlier band-structure results,[18−21] Fig. 2 indicates that polysilane is a direct-gap material with the band gap occurring at the edge of the unfolded Brillouin zone for all three conformations. We find that
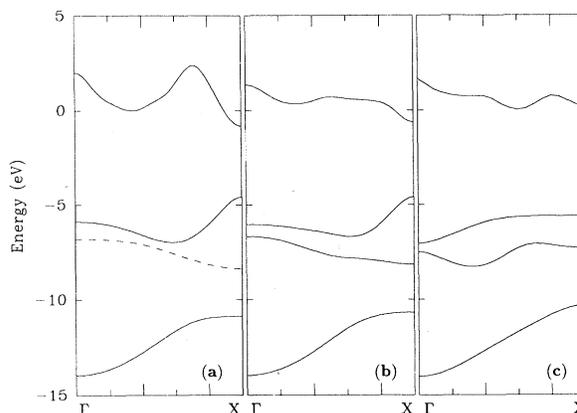
FIG. 2. Band structure for different conformations of unsubstituted polysilane using the LCAO-LDF method. Top band in all curves is unoccupied, with the Fermi level at midgap between top band and highest occupied band. (a) all-trans conformation. σ-like bands are denoted with solid lines, π-like bands with dashed lines. (b) 7/3 helical conformation. (c) 4/1 helical (all-gauche) conformation.

the band gap increases with decreasing dihedral angle, as given in Table I. As noted by other workers,[19−21,23−25] the states immediately below and above the Fermi level are predominantly silicon-silicon bonding and antibonding states, respectively, with the highest occupied valence-band state having only p-orbital contributions from the silicon sites. In the all-trans conformation, where the chain possesses C_{2v} symmetry about the silicon nuclei, the state immediately below the Fermi level will belong to the b_1 irreducible representation—symmetric with respect to reflection about the plane of the silicon backbone and antisymmetric with respect to reflection about the plane defined by a Si site and the two adjacent H sites. The lowest unoccupied state immediately above

TABLE I. One-electron energy levels of unsubstituted polysilane, $(SiH_2)_n$, and polydimethylsilane, $(SiMe_2)_n$, for top of occupied valence band (HOMO) and bottom of unoccupied conduction band (LUMO), resulting band gap E_g, and variation with conformation relative to E_g at the all-trans conformation. Results in parentheses are for calculations using larger $10s\,6p\,1d\,/3s$ basis set. All energies are reported in eV.

Conformation:	all-trans		7/3 helix	4/1 helix	
Dihedral angle (deg):	180		148.8	62.7	
$(SiH_2)_n$					
LUMO	−0.83	(−1.25)	−0.64	+0.21	(−0.02)
HOMO	−4.58	(−4.78)	−4.58	−5.60	(−5.60)
E_g	3.75	(3.52)	3.94	5.81	(5.58)
ΔE_g	0.0		0.19	2.06	(2.06)
$(SiMe_2)_n$					
LUMO	−0.10	(−0.59)		+1.10	
HOMO	−2.94	(−3.23)		−3.72	
E_g	2.84	(2.64)		4.82	
ΔE_g	0.0			1.98	

the Fermi level will belong to the totally symmetric a_1 representation. As the dihedral angles decrease and the silicon backbone becomes more twisted, the C_2 subgroup remains present and requires that the occupied and unoccupied frontier states at the Brillouin-zone edge remain, respectively, in the b and a irreducible representations of the C_2 group. Thus, as found in the calculations presented herein and similar work using semiempirical methods,[33] the s orbitals on the silicon nuclei will not contribute, by symmetry, to the highest occupied state in the valence band in any reasonable helical conformation maintaining the C_2 symmetry.

Figure 3 depicts the band structures for the all-trans conformations of PS and PDMS using the $10s\,6p\,1d$ / $7s\,3p$ /$3s$ basis set. We find that the addition of methyl substituents leads to a decrease in the band gap for this basis set from 3.52 to 2.64 eV, and from 3.75 to 2.84 eV using the minimal orbital basis set. Similar calculations on an all-trans conformation of polydiethylsilane using the minimal basis set yield a band gap of 2.56 eV. Local-density-functional methods typically underestimate the band gaps of polymeric materials by 30–50 %;[34–37] the first-principles result is thus consistent with the experimentally suggested gap for PDMS of 4.2 eV.[15] Most of the shift in gap between PS and PDMS appears to be attributable to the upward shift of the valence-band edge, which is largely caused by mixing with lower-lying C—H bonding bands introduced by the methyl substituent. These states can be seen lying in the vicinity of -10 eV in Fig. 3(b). Other than this shift in gap, no major changes apparently occur in the frontier states immediately about the Fermi level in the valence and conduction bands of PDMS relative to those of PS.
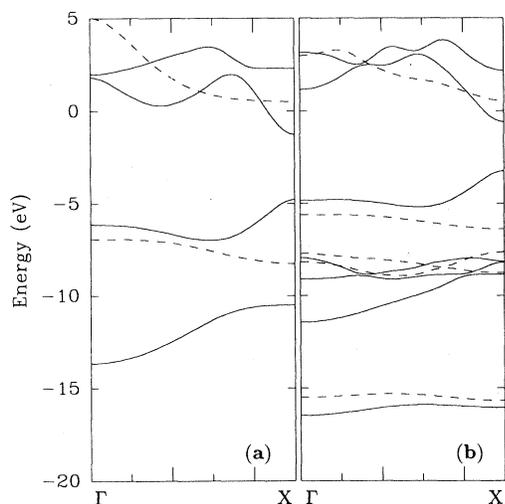
FIG. 3. Band structure for all-trans conformations of (a) unsubstituted polysilane and (b) polydimethylsilane using the LCAO-LDF method with $10s\,6p\,1d$ /$7s\,3p$ /$3s$ orbital basis. σ-like bands are denoted with solid lines, π-like bands with dashed lines. The Fermi levels for both sets of curves lie at midgap between -2 and -3 eV.
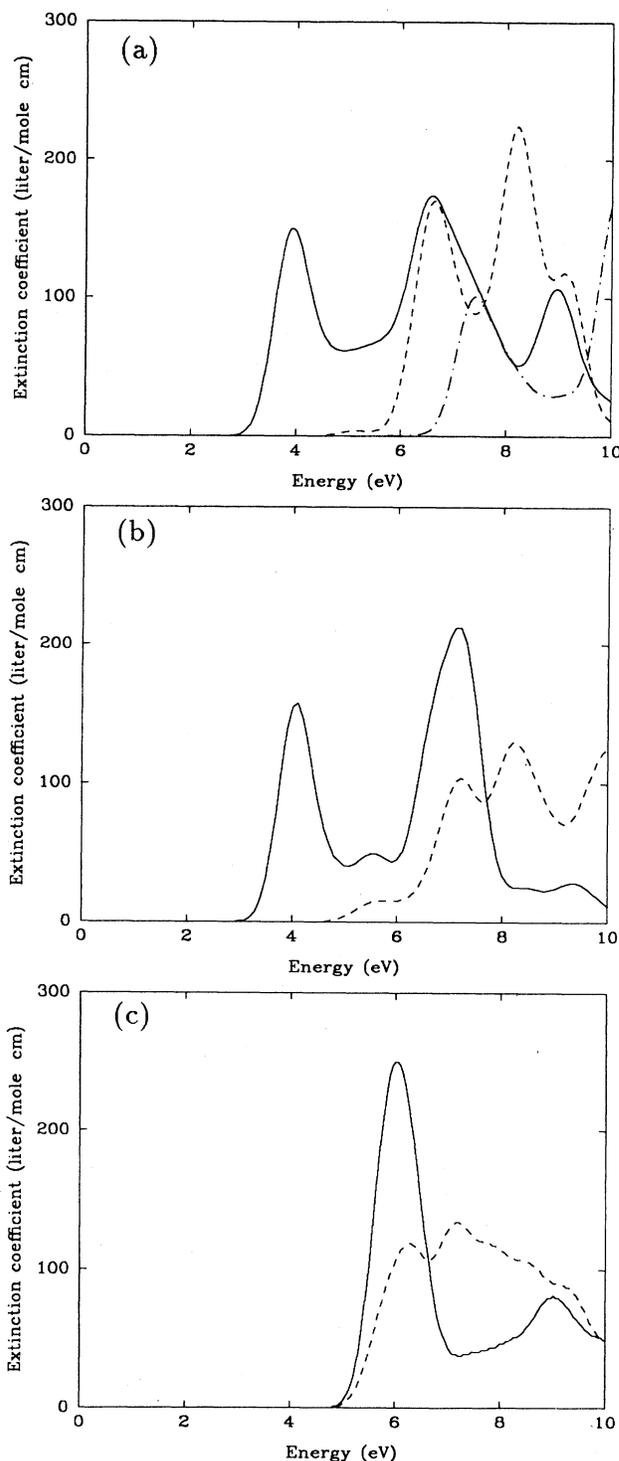
FIG. 4. Calculated absorption spectra for different conformations of unsubstituted polysilane: (a) all-trans, (b) 7/3 helix, and (c) 4/1 helix. Solid lines denote absorption for polarizations parallel to the chain axis, dashed-dotted lines denote absorption for polarizations perpendicular to the plane of the silicon backbone (for the all-trans conformation only), and the dashed lines denote the remaining polarization perpendicular to the chain axis.

As given in Table I, the band gap in PDMS increases by 1.98 eV on going from the all-trans conformation to the 4/1 helix, roughly the same as that found in PS.

Figure 4 depicts the calculated absorption spectra for the three helical conformations of PS; Fig. 5 depicts these spectra for the all-trans and 4/1 helical conformations of PDMS. The quantity directly calculated is the optical conductivity $\sigma_i(\omega)$ for the three polarization directions using oscillator strengths calculated for direct interband transitions (within the original or "folded" one-dimensional Brillouin zone constructed using the translational group symmetry) and neglecting local-field effects,[28] with the depicted extinction coefficients given by $\sigma_i \Omega/c$, where σ_i is the calculated optical conductivity, Ω is the volume per silicon nucleus, and c is the speed of light in vacuum. Although the absolute magnitudes of the predicted extinction coefficients are not in particularly good agreement with experimental results, this approach does allow us to analyze the expected line shape and compare differences between similar polymeric systems. We have found that this approach yields excellent results for π-conjugated polymers such as polyacetylene. The three curves in Figs. 4(a) and 5(a) for the all-trans conformations correspond to the polarization parallel to the chain axis (solid lines), the polarization perpendicular to the plane of the silicon-backbone nuclei (dashed-dotted lines), and the remaining polarization in the plane of the silicon backbone (dashed lines). For the helical conformations the results for the two perpendicular polarizations are equivalent.
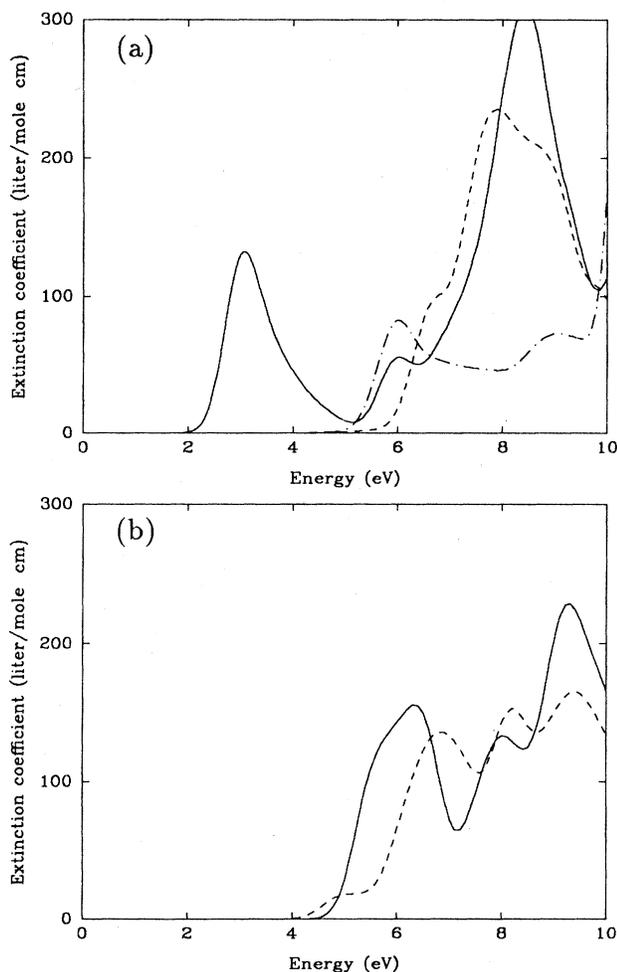
The dominant low-energy feature of the absorption spectra of the all-trans conformations is the strong absorption peak for polarizations parallel to the chain axis. This peak arises from excitations between the states at the top of the valence band and the bottom of the conduction band. Because these two states differ in parity with respect to the C_2 rotation axis about each silicon, large on-site matrix elements occur for the interband transition oscillator strengths for polarizations parallel to the chain axis. We see that as the silicon backbone becomes more helical, the absorption threshold and peak move in line with the increase in band gap, with an additional trend towards less anisotropic absorption. The observed behavior for PDMS is similar, with the low-energy peak arising from the same origins as in PS, but with additional structure above this threshold peak caused by excitations between the states near the Fermi level introduced by the addition of the methyl substituents.

DISCUSSION

The bands for PS in Fig. 2 can be interpreted effectively using an sp^3 hybrid model for the silicon backbone. Such models have long been found useful in modeling the electronic structure of polysilane systems, from early work[17] using the Sandorfy C method[38] to study conjugative effects in polysilane oligomers, to more recent work[26] studying possible polaronic effects in the excitation spectra of these materials. Within such a model, the lowest two bands in Fig. 2 can be assigned to Si—H bonding bands, with the silicon contribution predominantly originating from the silicon sp^3 hybrids along the Si—H bonds. The lowest band [the σ band in Fig. 2(a) for the all-trans conformation] is thus primarily the symmetric combination of these two silicon sp^3 hybrids in a bonding arrangement with the hydrogen s orbitals; the second-lowest band [the π band in Fig. 2(a)] is primarily the equivalent antisymmetric combination in a bonding arrangement with the hydrogen s orbitals.

A reasonable model can be constructed for the valence- and conduction-band states in the vicinity of the Fermi level by further assuming that these states are strictly constructed from a basis of the two sp^3 hybrid orbitals per silicon aligned in the directions of the silicon-silicon bonds. Such a model Hamiltonian (for a reasonable choice of parameters) predicts a band gap at the

FIG. 5. Calculated absorption spectra for different conformations of polydimethylsilane: (a) all-trans, and (b) 4/1 helix. Solid lines denote absorption for polarizations parallel to the chain axis, dashed-dotted lines denote absorption for polarizations perpendicular to the plane of the silicon backbone (for the all-trans conformation only), and the dashed lines denote the remaining polarization perpendicular to the chain axis.

Brillouin-zone edge with the occupied state immediately below the Fermi level (assuming two electrons per site) being a combination of sp^3 hybrids that is antisymmetric about the silicon site—and consequently of p-orbital character only—but bonding with respect to the adjacent silicon sp^3 hybrids. The unoccupied state in the conduction band immediately above the Fermi level will be the combination symmetric about the silicon site and antibonding with respect to the adjacent silicon hybrids, and will be a mixture of s- and p-orbital character. The only interaction between hybrid orbitals on adjacent sites (assuming a nearest-neighbor approximation) that is dependent on the dihedral angle of the backbone will be the 1-4 interaction[25,39] between exterior sp^3 hybrids. This interaction stabilizes the occupied antisymmetric state, destabilizes the unoccupied symmetric state, and increases in strength with decreasing dihedral angle. Thus, the band gap will increase as the silicon backbone is twisted from the all-trans conformation. The form of the band gap E_g within the hybrid model and using conventional nomenclature for the interatomic matrix element yields

$$E_g = \frac{2}{1+\xi}|(\varepsilon_s - \varepsilon_p)\xi - (1+\xi^2)V_{pp\sigma} - 2\xi^{1/2}(1-\xi)V_{sp\sigma}$$
$$-2\xi V_{ss\sigma} - (1-\xi^2)V_{pp\pi}\cos\phi| , \qquad (1)$$

where $\xi \equiv -\cos\theta$, θ is the silicon-backbone bond angle, and ϕ is the silicon-backbone dihedral angle. Given a fixed bond angle θ, the change in band gap as a function of ϕ therefore only depends on the adjacent p-orbital π-interaction parameter $V_{pp\pi}$.

Because E_g is the sum of several terms of opposite sign and dependent on six independent parameters, the magnitude of the band gap is quite sensitive to choice of parameters; i.e., we do not expect that E_g calculated using Eq. (1) with generally available parameters such as Harrison's universal values[40] would necessarily yield a value in close agreement with more sophisticated theoretical methods or with experiment. The variation in gap with dihedral angle, however, depends linearly on a single parameter, $V_{pp\pi}$, and we would thus expect this model to yield a quite reasonable prediction of the variation in gap and to be relatively insensitive to the choice of other tight-binding parameters.

The first-principles results obtained for polysilane strongly support the applicability of such a tight-binding model for the frontier states of these materials. Qualitatively the states calculated using the LCAO-LDF method agree closely with those predicted using the above model. The highest occupied valence-band state at the edge of the Brillouin zone is totally composed of silicon p orbitals for the all-trans conformation and remains predominantly composed of p orbitals for each silicon site that lies along a direction vector defined by the line segment connecting the two neighbor silicon sites. The Mulliken population analysis indicates that the silicon population of the top valence-band state decreases from 100% for the all-trans conformation to roughly 91% for the 4/1 helical conformation. Likewise, the state at the bottom of the conduction band is predominantly an sp hybrid state with the major lobe pointing away from the hydrogens along

the bisector of the two Si—Si bonds, and with the silicon population almost exactly 100% for all three conformations.

In addition to this qualitative agreement, the variation of the band gap with dihedral angle calculated using the LCAO-LDF method also agrees quanitatively with the variation predicted by the tight-binding method. Harrison's universal values for interatomic matrix elements yield $V_{pp\pi} = 1.12$ eV for a Si—Si bond distance of 2.35 Å. The corresponding variation in E_g (relative to the all-trans conformation, $\phi = 180°$) calculated using Eq. (1) for a bond angle $\theta = 111.7°$ is 0.2 eV for the 7/3 helix and 2.1 eV for the 4/1 helix. As can be seen in Table I, these values are in very good agreement with those obtained by the first-principles method.

These results are, in large part, supportive of current interpretations of experimental results for dialkyl-substituted polysilanes. As the temperature is lowered, PDHS is believed to undergo a phase transition from a disordered state with a λ_{max} of ~ 315 nm (4.0 eV) in both solid-film form and solution[8-12] to an ordered phase with a λ_{max} of 355 nm (3.5 eV) in solution[8,9,12] and 374 nm (3.3 eV) in solid films,[10,11] leading to a red shift of the absorption peak of 0.4–0.6 eV. X-ray diffraction and other spectroscopic measurements[13,14] suggest that the low-temperature equilibrium phase of PDHS in solid films is a highly crystalline, all-trans planar zigzag conformation with silicon-backbone bond angles of roughly 120°. Polarized absorption spectra of stretch-oriented samples of PDHS exhibit threshold absorbance only for polarizations parallel to the stretch (and presumably the chain-axis) direction.[12] More recent results for shear-oriented samples of PDHS exhibit a similar strongly polarized threshold absorption.[41]

The spectra for the disordered state are believed to arise from excitations in a rotationally disordered silicon backbone, with a thermal distribution of trans and gauche conformers along the chain.[41,42] Recent theoretical work using semiempirical treatments of finite chains suggests that the low-energy excitations of a disordered polysilane chain would tend to localize in regions of consecutive trans conformations, with even two to three adjacent trans conformations sufficient to allow a local excitation roughly midrange between that of the all-trans and the all-gauche backbone conformation.[25] We would, therefore, expect the observed shift in absorption maxima between the all-trans phase and the disordered phase to be a major fraction of the shift expected between the two extreme conformations of the all-trans conformation and the all-gauche 4/1 helical conformation. Based on such an argument, we find that our calculated shift of ~ 2 eV for the absorption thresholds and the major calculated threshold absorption peaks in both PS and PDMS between these two conformations is thus in qualitative agreement with the experimentally observed shift of ~ 0.5 eV between the disordered and highly ordered phases of PDHS. In addition, our calculated results for the optical-absorption spectra are consistent with the observed absorption anisotropy in oriented samples of PDHS.[12,41]

Recent experimental results for PDPS are more

difficult to interpret in terms of the above theoretical calculations. In solid films, PDPS is believed to undergo a similar transition to a 7/3 helical from with a λ_{max} of 313 nm (4.0 eV),[15,16] roughly a 0.6-eV blue shift relative to that expected for the all-trans conformation of PDHS. Because this shift arises from differences between the absorption spectra of the ordered phases of PDHS and PDPS, our theoretical results should be directly comparable for this value, as opposed to the shift between ordered and disordered phases for which we can only make a qualitative comparison. The calculated first-principles results for both the band gap and the optical-absorption spectra of the all-trans and 7/3 helical conformations of PS would suggest that a 0.6-eV shift is roughly 3 times larger than one would expect for a straightforward change of the backbone dihedral angles without additional modification of the backbone. Such a conclusion is supported by the agreement of the tight-binding model quantitatively, and by the qualitative prediction of the tight-binding model that the $\cos\phi$ dependence on the variation of the gap with ϕ should lead to small, second-order changes in the gap and related observed quantities such as λ_{max} for small deformations of the backbone from the all-trans conformation.

Further evidence supporting the expected strong dependence on steric interactions between substituents of the equilibrium structure of such a chain is provided by the small energy differences between trans and gauche conformations obtained by both *ab initio*[24] and semi-empirical[23] studies of polysilane oligomers, as well as empirical studies of alkyl-substituted systems.[43] The 7/3 helix thus might represent a relatively low-energy compromise that allows the reduction of steric repulsions between substituents on next-nearest silicon sites at the cost of only a slight deformation of the staggered all-trans conformation—which itself minimizes the steric interactions between substituents on adjacent sites. We could further speculate that these next-nearest-neighbor steric interactions lead to larger equilibrium silicon-backbone bond angles in the all-trans conformation than in the 7/3 helix, and that this effect would be accentuated in systems with bulky substituents.

With this in mind, we note that *ab initio* calculations on polysilane oligomers[24] suggest an equilibrium backbone bond angle of roughly 112°. According to the above speculation, the experimentally estimated bond angle for the all-trans phase of PDHS of 120° arises from repulsive interactions between silicon substituents on next-nearest backbone silicons. To test the reasonableness of this idea, *ab initio* calculations were carried out on trisilane (S_3H_8, the smallest silane oligomer having a silicon-backbone bond angle) and propane (C_3H_8, the carbon analog) using a 6-31 G* basis set.[44] Full geometry optimizations were carried out for a set of given bond angles. The equilibrium bond angles were 112.7° for trisilane and 112.8° for propane. The total-energy difference between the equilibrium conformation and a conformation with a fixed 120° bond angle with all other parameters reoptimized is 1.3 kcal/mole (0.054 eV) for propane but only 0.4 kcal/mole (0.019 eV) for trisilane. These calculations are suggestive that steric repulsions in silicon backbone systems could

be easily sufficient to produce an increase in the silicon-backbone bond angle of the magnitude suggested for PDHS.

We might, therefore, expect to find a reduced backbone bond angle in the 7/3 helical conformations compared to those found in the planar zigzag conformations. A LCAO-LDF calculation for the all-trans conformation of PS using a backbone bond angle of 120°, with all other bond distances and bond angles the same as in our earlier calculations and using the $10s6s1d/3s$ orbital basis set, yields a band gap of 3.3 eV compared to the gap of 3.5 eV obtained from an equivalent calculation using the bond angle of 111.7 eV. We can further speculate then that the blue shift of the low-temperature solid-film λ_{max} of roughly 0.6 eV on going from PDHS to PDPS might well result from nearly equal contributions from the change in backbone dihedral angle and from the relaxation of backbone bond angle caused by decreasing substituent repulsions as the backbone becomes more helical.

SUMMARY

In general, we have found that these first-principles results support previous theoretically and experimentally based interpretations of the nature and behavior of the electronic states in the vicinity of the Fermi level in the organopolysilanes. First, consistent with a broad range of theoretical studies, the first-principles results predict that these materials are direct-gap insulators, with the low-energy excitation being a σ-σ^* transition. Both the highest occupied and lowest unoccupied states are silicon bonding and antibonding states, and can be treated to an excellent approximation using a tight-binding model with two sp^3 hybrids per silicon. Such a model also describes well the change in band gap as the backbone is twisted from the all-trans conformation (or as the backbone dihedral angles are decreased from 180°), which arises from the 1-4 interaction in the sp^3-hybrid model.

We find that these frontier states and their associated behavior remain essentially unchanged upon methyl substitution of the silicon backbone. We do find that the addition of methyl substituents can directly reduce the band gap from mixing of alkyl-substituent states and the silicon-backbone states, although the additional results for the all-trans conformation of polydiethylsilane suggest that the behavior experimentally observed for larger substituents probably arises indirectly from the steric effects of the substituents on the backbone conformation. Both the band-gap results and the theoretically predicted absorption spectra as a function of backbone dihedral angle are strongly supportive of current interpretations of the spectra of PDHS. Our results are less supportive of current ideas of the shift in λ_{max} for the low-temperature equilibrium conformation of PDPS relative to PDHS arising directly from torsional changes in the silicon backbone, and lead us to surmise that the observed differences in electronic structure may arise from more complicated effects in the change in backbone conformation caused by the order-disorder transition than those of just a change in backbone dihedral angle. Our current

theoretical results cannot provide us with an enequivocal answer to this question, and a more complete theoretical answer will probably require, at the least, reliable full-geometry total-energy optimizations for these materials.

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