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Energy-band structure of chainlike polysilane $(SiH_2)_n$ alloys

Kyozaburo Takeda and Nobuo Matsumoto
Musashino Electrical Communication Laboratory, Nippon Telegraph & Telephone Public Corporation,
Musashino-shi, Tokyo 180, Japan

Mitsuru Fukuchi
Department of Instrumentation Engineering, Faculty of Science & Technology,
Keio University, Yokohama 223, Japan

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The energy-band structure for ideal polysilane $(SiH_2)_n$ is calculated using the Slater-Koster linear combination of atomic orbitals (LCAO) method. The interatomic matrix elements are estimated by using Harrison's approximate representation. From the calculated band structure we deduce that chainlike polysilane is a semiconductor having a wide direct band gap and that optical transitions are allowed. This is consistent with the experimental results showing a wide optical gap and highly efficient luminescence in novel Si:H alloys, consisting of many polysilane chain segments.

I. INTRODUCTION

It has recently been reported[1–3] that binary Si:H alloys on low-temperature substrates, prepared by the plasma decomposition of disilane or by the homogeneous chemical vapor deposition (HOMOCVD) method, have a wider optical band gap than does amorphous hydrogenated silicon (*a*-Si:H) prepared by conventional methods. Moreover, the alloys show efficient visible photoluminescence, even at room temperature.

It is impossible to explain these experimental results if the novel Si:H alloys have an ordinary *a*-Si:H structure (whose band gap is less than 1.9 eV). In order to interpret the experimental results, the intrinsic band gap caused by the novel materials should at least be greater than the experimental band gap (2.45 eV).[3] A $(SiH_2)_n$ polysilane chain model[4–6] has been proposed for the microstructure of this novel binary material based on the results of hydrogen content measurements and infrared-absorption-spectrum analysis.[2,3] However, the electronic structure for polysilane has not been clarified.

This paper reports the calculated electronic structure for an "ideal" polysilane chain and discusses the origins of the wide band gap and efficient photoluminescence exhibited in this novel binary Si:H material. A semiempirical approach is used to calculate the energy-band structure based on the Slater-Koster (SK) linear combination of atomic orbitals (LCAO) (Ref. 7) method. The interatomic matrix elements are estimated by using Harrison's approach.[8,9]

II. OPTIMIZED GEOMETRY FOR POLYSILANE MOLECULAR $H(SiH_2)_nH$

According to the vibrational spectra,[4–6] the chainlike polysilane material is thought to be synthesized by the polymerization of several possible monomers of SiH_4, Si_2H_6, etc. Therefore, several intermediate $H(SiH_2)_nH$-type molecular products can be produced in the polymerization process of ideal $(SiH_2)_n$ materials. By using the conventional molecular orbital (MO) method, the authors first calculated the electron-energy eigenvalues for $H(SiH_2)_nH$ (in this work n ranges from 2 to 8). Next, the optimized atomic configuration for $H(SiH_2)_nH$ was determined by finding the minimum point of the total energy (sum of electron energy and repulsive energy between constitute nuclei) which was done by varying the atomic configurations for the virtual molecules.

The MO method used in this work is the complete neglect of differential overlaps (CNDO) approach, in which the self-consistent Hartree-Fock equation is solved semiempirically, as follows. Hartree-Fock matrix elements, F_{rs}, between r-type atomic orbitals (ϕ_r) and s-type atomic orbitals (ϕ_s) are given as follows:

$$F_{rs}=H_{rs}^{\text{core}}+\sum_{jtu} C_{tj}C_{uj}[2(rs\mid tu)-(rt\mid su)] , \tag{1}$$

where C_{tj} is the expansion coefficient corresponding to t-type atomic orbitals (t-AO's) and the electron repulsive integral $(rs\mid tu)$ is given as

$$(rs\mid tu)=\int \phi_{r(1)}\phi_{s(1)}\frac{1}{r_{12}}\phi_{t(2)}\phi_{u(2)}d\tau_{12} . \tag{2}$$

In the CNDO approach, differential overlaps are completely neglected. Thus F_{rs} is rewritten as

$$F_{rr}=H_{rr}^{\text{core}}+\tfrac{1}{2}P_{rr}(rr\mid rr)+\sum_{t\neq r} P_{tt}(rr\mid tt) ,$$

$$F_{rs}=H_{rs}-\tfrac{1}{2}P_{rs}(rr\mid ss) ,$$

where

$$P_{rs}=\sum_{j} C_{rj}C_{sj} . \tag{3}$$

Here, the AO's used were the same as those for $3s$, $3p_x$, $3p_y$, and $3p_z$ of Si and $1s$ of H atoms.

Figure 1 gives the resulting electron-energy levels with varying n for the corresponding optimized geometries of

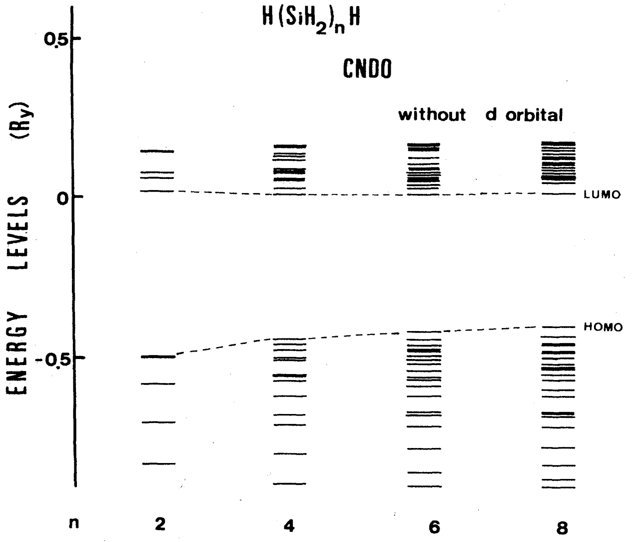


FIG. 1. Calculated electron-energy levels for $H(SiH_2)_nH$ monomer molecules with optimized geometry using the CNDO/MO method without *d* orbitals.

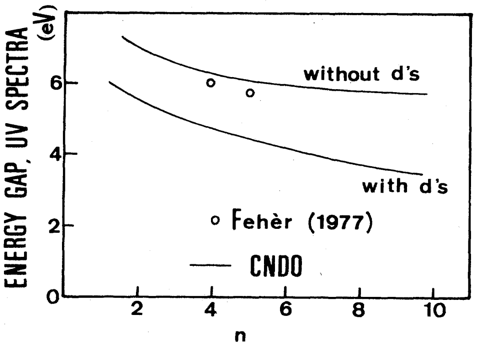
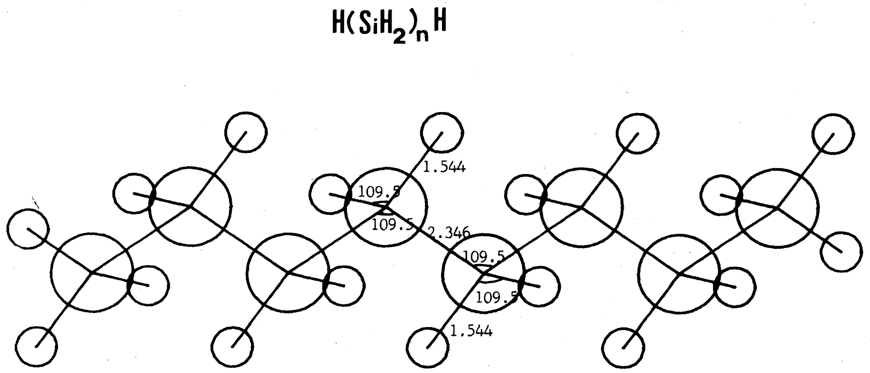


FIG. 2. Comparison of the calculated bathochromic shift with those experimental ones. The calculated values are obtained from the energy distance between the HOMO and LUMO state by the CNDO/MO calculation, in which the bases of Si 3*d* orbitals are included (with *d* orbital) or not (without *d* orbital). Experimental results are quoted from the results by Fehèr.

the $H(SiH_2)_nH$ molecule. The highest occupied molecular orbital (HOMO) state is composed of the bonding state between skeleton Si-3*p* AO's directed along the skeleton direction. The contribution from the terminated horn H atoms is sufficiently small to be neglected for this state. On the other hand, the lowest unoccupied molecular-orbital (LUMO) state is composed of the antibonding state between skeleton Si-3*s* and horn H-1*s* AO's. With the increase of the chain length, the energy difference between the HOMO and the LUMO state is reduced, which is experimentally observed as a bathochromic shift.

(a) tetrahedral geometry



(b) optimized geometry

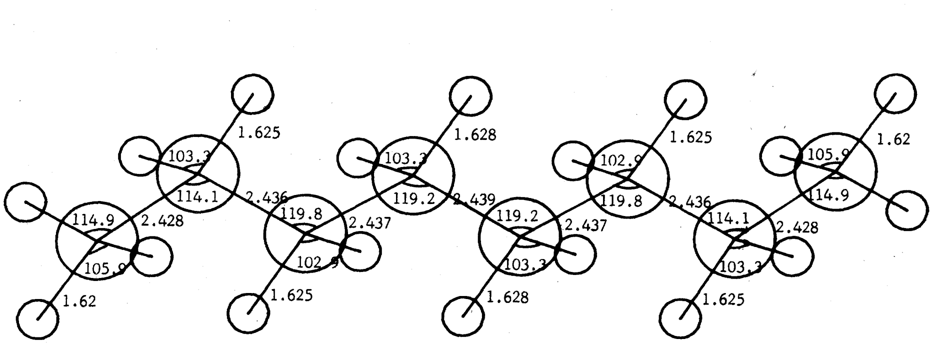


FIG. 3. Variation in the atomic configuration of $H(SiH_2)_8H$. (a) Tetrahedrally covalent configuration. (b) Optimized geometry by CNDO method without *d* orbitals. Values of Phillips rationalized radii of tetrahedral bonds were used as covalent bond lengths (a). The bond lengths and bond angles are shown in the figure in units of angstrom and degree, respectively.

Fehér[10] reported the experimental bathochromic shift of n-Si_3H_8 and n-Si_5H_{12} uv spectra. Figure 2 shows the comparison of the calculated bathochromic shift with those experimental results. The calculated bathochromic shift has a reasonable agreement with experiment results. The slight discrepancy found is that the experimental values are smaller than the calculated values without Si $3d$ orbitals, which suggests the possible existence of the d-state hybridization into the sp coupling.

The variation n in $H(SiH_2)_nH$-type molecules produces a change in the optimized geometries for the corresponding molecule. For instance, Figure 3 shows the variation in the atomic configuration of $H(SiH_2)_8H$ from the tetrahedrally covalent configuration [starting configuration, Fig. 3(a)] to the resulting optimized configuration [final configuration by optimized procedure, Fig. 3(b)]. From this result, the skeleton Si—Si of chainlike polysilane ($n = \infty$) appears to be planar, neglecting d orbitals.

The polymerization dependence of bond angles [α and β, Fig. 4(a)] and bond length [d_{Si} and d_H, Fig. 4(b)] were investigated. When index n becomes greater than 6, changes in both the bond angles and bond lengths are reduced. By extrapolating these values of finite monomer molecules, the optimized values can be derived for chainlike polysilane ($n = \infty$) as follows: bond angles $\alpha = 59°$ and $\beta = 52°$, and bond lengths $d_{Si} = 1.218$ Å and $d_H = 0.43$ Å. These semiempirical values were used as the optimized geometry for chainlike polysilane in later band calculations. This is because experimental structural analyses have not been carried out and the theoretical calculation for infinite n cannot be obtained directly.

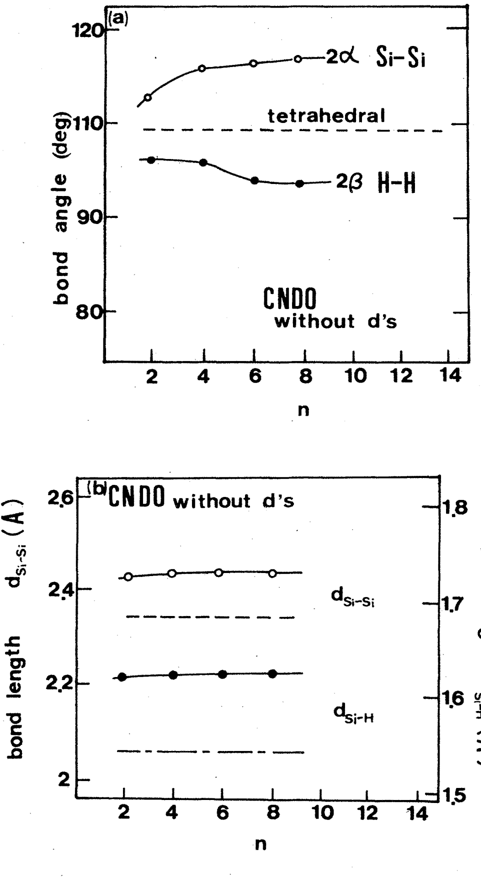


FIG. 4. Polymerization dependence of atomic geometry for $H(SiH_2)_nH$ using CNDO/MO methods without d orbitals. (a) Bond angles; ○ represents the bond angles 2α between Si—Si atoms and ● indicates those between H—H atoms. The tetrahedral angle is also shown as the broken line. (b) Bond length; ○ represents the bond length for d_{Si-Si} between Si—Si atoms and ● represents those for d_{Si-H} between Si—H atoms. Phillips rationalized values are also shown as — — — for d_{Si-Si} and —-—- for d_{Si-H}.

The variations in bond angles with n are more significant than variation in bond lengths. Since the structure for $H(SiH_2)_nH$ format molecular material is quasi one-dimensional and since the HOMO state is mainly constituted of p-like bonding states, electrons, in those states are localized along the molecular axis which is oriented in the skeleton atom directions. Therefore, the interatomic overlaps of the HOMO state are more easily varied by the changes in bond angles than those in bond lengths, which cause self-consistent changes in optimized molecular geometry. This introduces the prediction that the changes in atomic geometries affect the position of the valence-band edge in chainlike polysilane, comparatively more than they affect the position of the conduction-band edge. This explains the theoretical results reported by Ching *et al.*[11] and Allan *et al.*[12]

III. BAND STRUCTURE OF CHAINLIKE POLYSILANE

The electronic structure of infinite chainlike polysilane is calculated as follows. The atomic configuration is assumed to be as shown in Fig. 5 based on the results obtained for monomer molecules $H(SiH_2)_nH$. This configuration can be characterized by bond angles α and β and bond lengths d_{Si} and d_H because of the planar structure of the polysilane Si—Si skeleton chain. These Si—Si bonds are thought to be almost covalent which supports the concept that the energy-band structure can be estimated by the SK LCAO approach.

In the unit cell of this model, there are two silicon

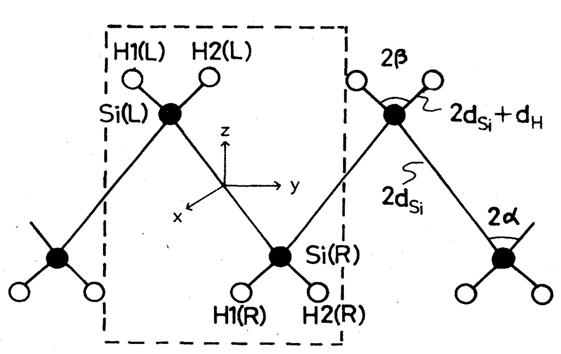


FIG. 5. Ideal structure for the polysilane $(SiH_2)_n$ chainlike model. The region enclosed by the dashed lines is the unit cell. ● indicate silicon atoms and ○ hydrogen atoms. The Si—Si chain skeleton is in the y-z plane and the horns of the H atoms, terminating at each silicon atom, are in the x-z plane.

atoms and four hydrogen atoms, named Si(R), Si(L), H1(R), H2(R), H1(L), and H2(L). Thus, the 12×12 secular equation should be solved for the 12 bases of R_S, R_X, R_Y, R_Z, L_S, L_X, L_Y, L_Z, R_{H1}, R_{H2}, L_{H1}, and L_{H2}, where the notation $R(L)$ refers to the right- (left-) hand-side atoms in the unit cell and the symbols S, X, Y, and Z correspond to the $3s$, $3p_x$, $3p_y$, and $3p_z$ atomic orbitals of silicon, respectively. Similarly, R_{H1},(L_{H1}) represents the $1s$ atomic orbitals of hydrogen, terminating at Si(R) [Si(L)].

Forming the Bloch sum $\sum_i e^{i\vec{k}\cdot\vec{\mathbb{R}}}\phi_i(r-\vec{\mathbb{R}}_l)$, where $\phi_i(\vec{\mathbf{r}}-\vec{\mathbb{R}}_l)$ $(i=R_S,\ldots,L_{\mathrm{H2}})$ is an atomic orbital located at a positional vector $\vec{\mathbb{R}}_l$ and whose sum is extended over the atoms in equivalent positions in all the unit cells of the crystal, the energy eigenvalues E can be obtained by solving the following secular equation:

$$\left|\epsilon_i\sum_l e^{i\vec{k}\cdot\vec{\mathbb{R}}_l}\langle\phi_j(\vec{\mathbf{r}}-\mathbb{R}_l)\,|\,\phi_i(\vec{\mathbf{r}})\rangle+\sum_l e^{i\vec{k}\cdot\vec{\mathbb{R}}_l}\langle\phi_j(\vec{\mathbf{r}}-\vec{\mathbb{R}}_l)\,|\,\hat{H}'\,|\,\phi_i(\vec{\mathbf{r}})\rangle-E\sum_l e^{i\vec{k}\cdot\vec{\mathbb{R}}_l}\langle\phi_j(\vec{\mathbf{r}}-\vec{\mathbf{R}}_l)\,|\,\phi_i(\vec{\mathbf{r}})\rangle\right|=0\,. \tag{4}$$

In Eq. (4), the three-center integrals are neglected and the difference in the two positional vectors ($\vec{\mathbb{R}}_i-\vec{\mathbb{R}}_j$ in SK notation is rewritten as $\vec{\mathbb{R}}_l$. The symbol ϵ_i represents energy eigenvalues for the nonperturbed Hamiltonian in which the approximate values of Herman-Skillman's atomic values[13] are used.

One of the most important problems in carrying out this approach is the determination of interatomic matrix elements $\langle\phi_j(\vec{\mathbf{r}}-\vec{\mathbb{R}}_l)\,|\,\hat{H}'\,|\,\phi_i(\vec{\mathbf{r}})\rangle$. Slater and Koster[7] used these elements as disposable constants, instead of computing the various integrals analytically, to be chosen so that they would fit the results obtained by other methods. Therefore, when using the SK LCAO method, it is desirable to know the energy eigenvalues at several points in the Brillouin zone. The resultant energy eigenvalues for this novel $(\mathrm{SiH_2})_n$ alloy, however, have not been reported either experimentally or theoretically. Therefore, the SK LCAO method cannot be applied in a straightforward manner to this polysilane alloy.

Following Harrison[8] and Froyen *et al.*,[9] the interatomic terms can be expressed approximately by using interatomic distance d as

$$\langle\phi_j(\vec{\mathbf{r}}-R_l)\,|\,\hat{H}'\,|\,\phi_i(\vec{\mathbf{r}})\rangle=E_{ij\kappa(uvw)}=\eta_{ll'm}\frac{\hbar^2}{m_0 d^2}\,, \tag{5}$$

where κ represents σ or π bonding. The subscripts u, v, and w in parentheses are direction cosines for the positional vector $\vec{\mathbb{R}}_l$. The symbols l and l' on the right-hand side mean the azimuthal quantum number for individual atomic orbitals labeled by $s\,(l=0)$ or $p\,(l=1)$, and m is the magnetic quantum number labeled by σ $(m=0)$ or π $(m=1)$. The parameter $\eta_{ll'm}$ is the Harrison coefficient. For typical atomic configurations, such as a diamond, simple cubic (sc), bcc or fcc crystal structures, Harrison[8] and Froyen *et al.*[9] obtained $\eta_{ll'm}$ values whose differences, depending on the atomic configuration, are not very great. Therefore, they introduced the universal values for $\eta_{ll'm}$ by adjusting the corresponding values for several kinds of crystal structures.

It should be discussed whether these Harrison universal values can be applied to polysilane structure. It would be a good approximation that, in the chainlike polysilane, several bonding properties of monomer molecules have been partly maintained because the chainlike material or polysilane is thought to be synthesized by the polymerization of several possible monomers $\mathrm{H(SiH_2)_nH}$. Most types of bonding properties in a polysilane unit cell (Fig. 5) can be described by investigating $\mathrm{Si_2H_6}$ monomers, if only first-neighbor interaction is considered. We estimated $\eta_{ll'm}$ values for polysilane by the help of MO approaches (CNDO and Hückel method). First, the Hamiltonian matrix elements for $\mathrm{Si_2H_6}$ monomers are calculated by the CNDO and Hückel approaches. Fitting those values with the corresponding Harrison approximate representations, the values of $\eta_{ss\sigma}$, $\eta_{sp\sigma}$, $\eta_{pp\sigma}$, and $\eta_{pp\pi}$ are determined.

When the Hückel matching approach is employed, another unknown parameter (the Hückel K value) should be determined. The MO calculation for $\mathrm{H(SiH_2)_nH}$ monomers shows that the lowest energy level for this type of molecule is constructed of $3s$ bonding states between the Si skeleton atoms. Therefore, Hückel's K value was determined such as $\eta_{ss\sigma}$ (to be estimated by the Hückel matching approach) is equal to -1.40 of Harrison's universal value. Other Harrison coefficient values are estimated by fitting the corresponding interatomic terms obtained by the Hückel MO method with the above K value.

Table I shows the resultant Harrison parameters calculated by the above two MO matching methods. The values $\eta_{ll'm}$, estimated from Hückel matching approach, have several disagreements with the universal values.

TABLE I. Harrison's coefficient values obtained by the MO matching approach compared with universal values.

	Simple Hückel	Nonoptimized CNDO	Optimized CNDO	Harrison's Universal value
$\eta_{ss\sigma}$	-1.4	-1.27	-1.51	-1.4
$\eta_{sp\sigma}$	1.3	1.39	1.83	1.84
$\eta_{pp\sigma}$	0.85	1.35	1.99	3.24
$\eta_{pp\pi}$	-0.48	-0.74	-0.81	-0.81

This is because electron-electron interactions are neglected in the Hückel MO method. When a nonoptimized CNDO fitting method is used, the inaccuracy of the molecular potential produces similar disagreements in the $\eta_{ll'm}$ values. Although polysilane has a quasi-one-dimensional crystal structure, the values $\eta_{ll'm}$ obtained by the optimized CNDO fitting method are almost equal to Harrison's universal values. The reason is that the crystal frameworks of polysilane are mainly constructed by skeleton Si sp^3 covalent bondings. The considerable disagreement of $\eta_{pp\sigma}$ is caused from the difference in atomic configuration between the infinite chainlike polysilane unit cell and the isolated finite length molecule (Si_2H_6). Skeath *et al.*[14] calculated the electronic structure of a Sb zigzag chain arrangement on GaAs (110) surfaces by using Harrison's universal values. The Si—Si skeleton of polysilane shows a stronger tendency toward sp^3 covalency than the Sb zigzag chain. For these two reasons, we also use the universal values for polysilane band calculations to avoid ambiguity in individual $\eta_{ll'm}$ values.

Resultant energy band structures are shown in Fig. 6 for the tetrahedral (a) and optimized atomic geometry (b). The chainlike $(SiH_2)_n$ binary alloy produces an energy-band gap. Therefore, it is classified as a "semiconductor" material. The top state of the valence band is derived by mixing a Si-$3p$ bonding state between $3p_y$ of Si(R) and $3p_y$ of Si(L). The bottom state of the conduction band is derived by mixing the Si-$3s$ and H-$1s$ antibonding state.

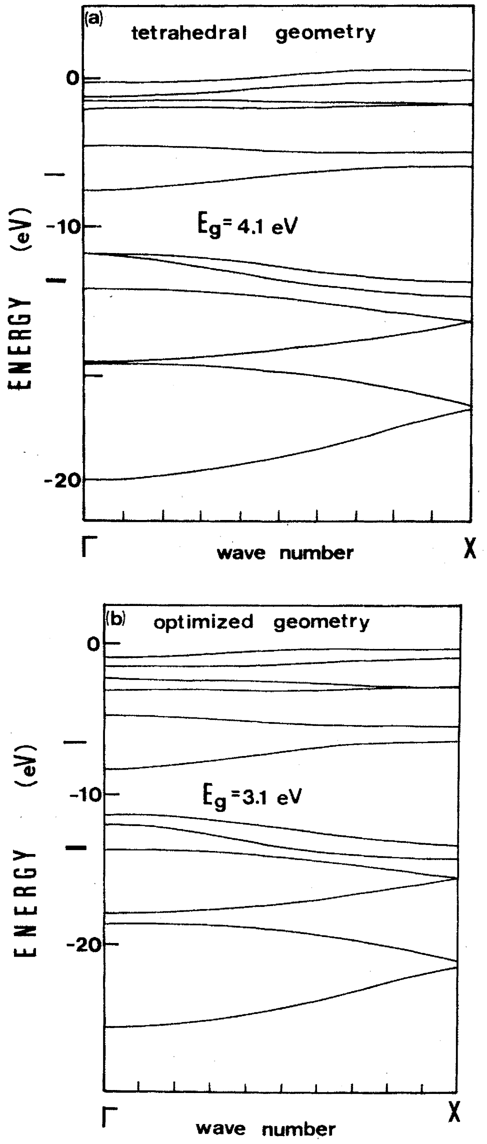


FIG. 6. Resultant energy-band structure. (a) For the tetrahedral covalent atomic configuration. Phillips values were used for bond lengths ($d_{Si}=1.173$ and $d_H=0.371$ Å). (b) Optimized atomic geometry deduced from the CNDO/MO method (Sec. II). Optimized bond angles are $\alpha=59°$ and $\beta=52°$ and those bond lengths are $d_{Si}=1.218$ and $d_H=0.43$ Å.

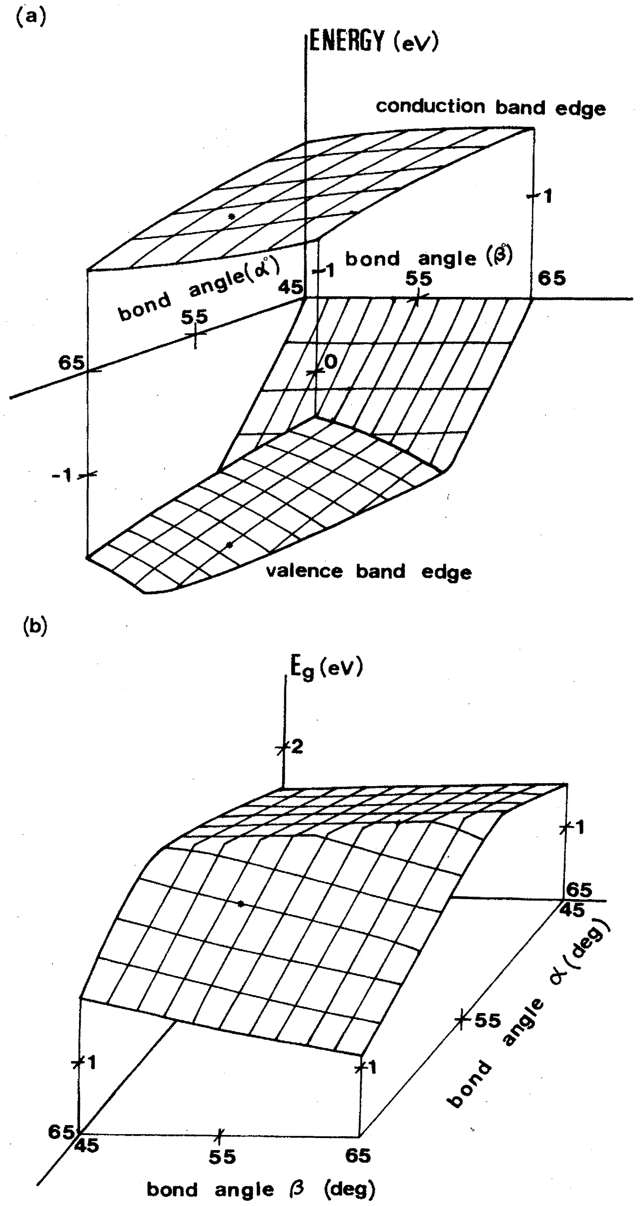


FIG. 7. Resulting band-structure map. (a) Band-edge dependence of bond angles α and β. Values of optimized bond lengths are used. * indicates the point of optimized geometry. (b) Band-gap dependence of bond angles α and β.

The resulting band structure shows a direct band gap and the difference in the parities between band edges. This enables the direct band-to-band optical transitions of electrons. The calculated direct band gap is 3.1 eV for the optimized atomic configuration, which is comparable with experimental wide band gaps.

The tetrahedral angles and optimized values deduced from the MO approach are the only stable bond angles for monosilane molecules[15,16] or finite monomer molecules, respectively. The valence-band top state is more greatly influenced by changes in the bond angles rather than in the bond lengths. Therefore, the band-structure dependence was investigated by varying bond angles (Fig. 7). Changes in the Si—Si bond angle α, compared with those in H—H bond angle β, cause greater variation in the band-edge energy positions. For a very wide range of α and β, the following property is, however, maintained; the directly allowed optical transition caused by both the direct band-gap structure as well as the different parities between band edges. This partly supports the experimental results which show that the novel binary $(\mathrm{SiH}_2)_n$ alloys give efficient photoluminescence even at room temperature.

Figure 8 shows the density of states (DOS) corresponding to Fig. 6(b). The typical energy dependence for DOS found in one-dimensional materials indicates both the divergence of the density of states at band edges and the decreases in them with increasing energy from band edges. The experimental results, however, have not yet confirmed these theoretical predictions.

The novel Si:H alloy obtained through recent experiments is thought to be a group of various finite-length polysilane chains distributed randomly in an *a*-Si network. The rotational barrier of SiH_3 parasol of $\mathrm{Si}_2\mathrm{H}_6$ is about one half smaller than that of $\mathrm{C}_2\mathrm{H}_6$ [0.053 eV (Ref. 17) for disilane and 0.12 eV for ethane].[18] This also produces many rotamers of polysilane chains and deformed chains. Therefore, the above conclusion for the ideal polysilane must be modified as follows. The presence of tail states originating from randomness reduces the band gap. Finite lengths and the random distribution of polysilane chains eliminate the divergence of the DOS. One should, moreover, consider the interaction between those randomly arranged polysilane chains and the effect of those polysilane chain mixing in an *a*-Si matrix. Qualitative coincidence between theory and experiments should be performed by both efforts of ideal polysilane preparations and calculations for "real" structural polysilane.

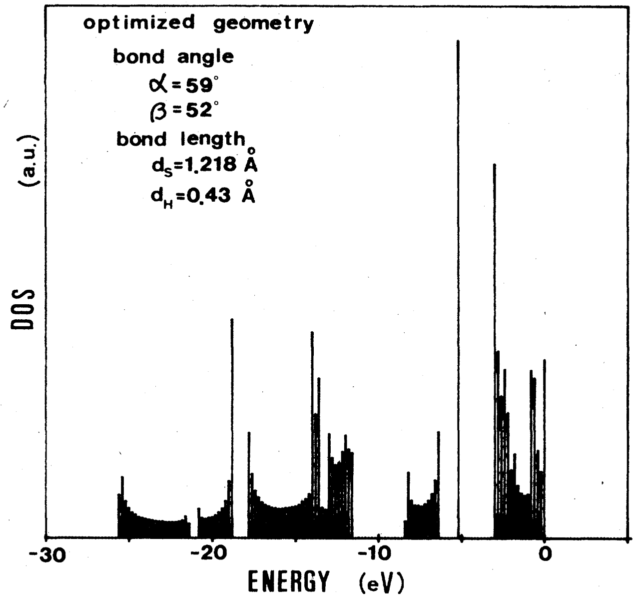


FIG. 8. Calculated density of states, corresponding to the energy-band structure in Fig. 6(b). Underestimation of atomic interaction between skeleton Si and horn H atoms produces slight differences in conduction-band structures from results by Allan and Jannopoulous (Ref. 12).

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[1] D. J. Wolford, B. A. Scott, J. A. Reimer, and J. A. Bradley, *Sixteenth International Conference on the Physics of Semiconductors, Montpellier, 1983* [Physica **117B&118B**, 920 (1983)].

[2] D. J. Wolford, J. A. Reimer, and B. A. Scott, Appl. Phys. Lett. **42**, 369 (1983).

[3] S. Furukawa and N. Matsumoto, Solid State Commun. **48**, 539 (1983).

[4] M. H. Brodsky, M. Cardona, and J. J. Cuomo, Phys. Rev. B **16**, 3556 (1977).

[5] B. von Roedern, L. Ley, and M. Cardona, Phys. Rev. Lett. **39**, 1576 (1977).

[6] G. Lucovsky, R. J. Nemanich, and J. C. Knights, Phys. Rev. B **19**, 2064 (1979).

[7] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[8] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1979).

[9] S. Froyen and W. A. Harrison, Phys. Rev. B **20**, 2420 (1979).

[10] F. Feher, Forschungsber. Landes Nordrhein-Westfalen No. 2632 (1977).

[11] W. Y. Ching, D. J. Lam, and C. C. Lin, Phys. Rev. B **21**, 2378 (1980).

[12] D. C. Allan and J. D. Jannopoulous, Phys. Rev. Lett. **44**, 43 (1980).

[13] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, Englewood Cliffs, 1963).

[14] P. Skeath, C. Y. Su, W. A. Harrison, I. Lindau, and W. E. Spicer, Phys. Rev. B **27**, 6246 (1983).

[15] J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).

[16] G. W. Bethke and M. K. Wilson, J. Chem. Phys. **26**, 1107 (1957).

[17] M. Pfeiffer and H. J. Spangenberg, Z. Phys. Chem. (Leipzig) **232**, 47 (1966).

[18] O. Bastiansen, H. M. Seip, and J. E. Boggs, *Perspectives in Structural Chemistry* (Wiley, New York, 1971), p. 97.