Theoretical Study on the Electronic Structure of Si–Ge Copolymers

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Abstract: The electronic structures of polysilane, polygermane, and their copolymers have been calculated by the first principle local density functional method. Polysilane and polygermane with trans-planar skeleton have direct band gaps of 3.89 and 3.31 eV, respectively. This direct-type band structure is conserved independently of the skeleton forms and the copolymerization. The ordered regular and/or block Si–Ge copolymerization introduces the zone-folding image in the copolymer band structures. Si_mGe_n ordered copolymers have the potential to be the *1D superlattice high polymers*. For Si–Ge copolymers having over five blocks, the band-edge electronic structure can be approximately estimated by using the effective mass theory, and a picture of a 1D-QW wire model can be imaged. Typical characteristics in the superlattice, the energy gaps, and optical transition profiles are theoretically discussed.

1. Introduction

Recently, there has been an increase in interest in organo-polysilanes not only in the field of science but also in engineering,[1] e.g., their application to photoresistance[2] and their semiconducting properties with regard to doping,[3] photoluminescence,[4] and photoconductivity.[5-7] Success in synthesizing soluble organopolygermanes will extend the above interests into group IV skeleton polymers.[8]

Fujino et al. synthesized an alternating organopolysilane, where different side chains are alternately substituted.[9] Trefonas et al. succeeded in synthesizing Si–Ge copolymers whose skeleton is formed of Si and Ge.[8] The catenation of Si and Ge atoms is not ordered but is disordered at the present time. However, the success in synthesizing the alternating block polymers or Si–Ge copolymers means that the potential profile along the skeleton can be modified indirectly by substituting side chains or directly by substituting skeleton atoms, respectively. Considering this point and the one dimensionality of a polymer, Matsumoto et al. suggested the possibility of creating a 1D superlattice by synthesizing Si–Ge heterocopolymers.[10]

The mesoscopic system of the 1D superlattice and 1D quantum wires has the modulated electronic structure, which causes novel optical absorption spectra and luminescence.[11,12] In the system for the compound semiconductors, quantum ballistic transports[13,14] and quantum interference effects have been actually reported.[15]

Table I. Guassian Exponents of Si 3s, 3p; Ge 4s, 4p; and H 1s AO's

atomic orbital	α_1	α_2	α_3
Si 3s	0.9764	0.3070	0.1009
Si 3p	0.3215	0.1114	
Ge 4s	0.15360	0.2505	0.0654
Ge 4p	1.8210	0.2472	0.0646
H 1s	1.3325	0.20153	

These mesoscopic systems produce many interests in the field of electron wave device engineering,[16] as well as in physics.[15] Here, we investigate theoretically the electronic structure of polysilane, polygermane, and their copolymers, focusing on whether copolymerization of heteroatoms will result in *1D superlattice high polymers*.

2. Methodology

Present band calculations are performed with the first principle local density functional (LDF) method.[17-20] The norm-conserving pseudopotential introduced by Hamann et al.[21,22] is used, in which the core basis functions are neglected in the calculation. The exchange-correlation energy is approximated by the functional form of Ceperley and Alder's[23] potential parametrized by Perdew and Zunger.[24]

The Bloch function is, here, expressed by the LCAO form of the pseudoatomic wave function, which is obtained numerically in terms of the sum of Gaussian-type orbitals (GTO's).[19,20] We determined the parameters of the expansion coefficients and the Gaussian exponent α_i by the least-squares fit method. Si 3d and Ge 4d orbitals are neglected in the present calculations because these GTO basis without d orbitals accurately reproduces consistent band structures of crystalline Si and Ge having an indirect band gap of 0.7 and 0.3 eV, respectively. Moreover, the significant changes have not been found in the electronic structures for the parent polymer calculations even when d orbitals are included. In the discussion of the valence band and also the lower conduction band (within a few electronvolts from the LUCB), the influence from the higher orbitals of Si 3d or Ge 4d AOs seems to be small enough to be negligible in the present LDF calculation.[25] Table 1 shows the values

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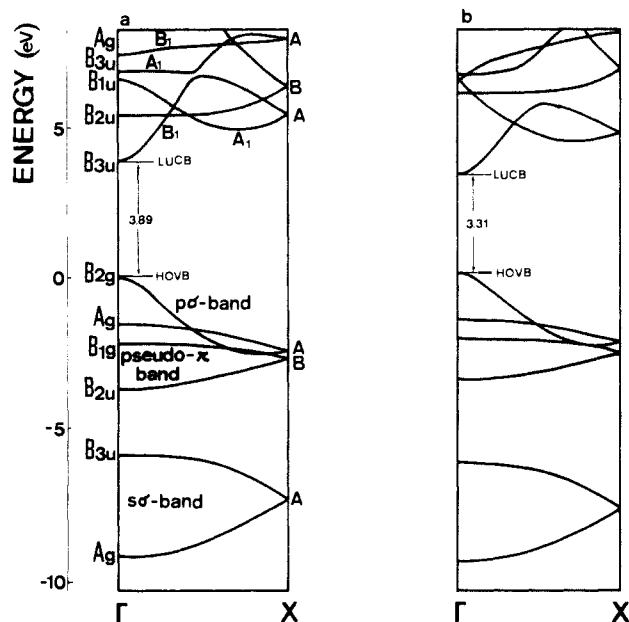
Figure 1. Electronic structures of parent polysilane $(SiH_2)_n$ (a) and polygermane $(GeH_2)_n$ (b) with a trans-planar zigzag form. The states are labeled by the D_{2h} point group's irreducible representations. The lower screened band corresponds to pseudo-π band and the upper to pseudo-π^* band. The energy scale is represented from HOVB in electron volts.

Figure 2. Electronic structures of parent polysilane $(SiH_2)_n$ (a) and polygermane $(GeH_2)_n$ (b) with a gauche-helix skeleton. The energy scale is represented from HOVB in electronvolts.

of Gaussian exponents used in this calculation. Details of the present LDF method were described in our previous paper.[26]

The practical SCF condition in the present calculation is

$$\int |V^{(n)}_{total}(r) - V^{(n+1)}_{total}(r)|^2 \, dr \le 1.0 \times 10^{-10} Ry^2 \qquad (1)$$

For the reciprocal lattice space integral, four special points were chosen for the 1D-reduced Brillouin zone. The real-space integration for the band calculation is performed by dividing the unit cell into a 40 × 80 × 80 mesh. The bond lengths are quoted from Phillips' rationalized values,[29] and all the atoms are assumed to be tetrahedrally bonded for simplification.

3. Parent homopolymers

3.1. Polysilane and Polygermane.
Figure 1 shows the calculated electronic energy structure of the parent homopolymers, polysilane[26] and polygermane, whose skeleton is assumed to form a trans-planar zigzag.[27] Both homopolymers show an analogous "directly allowed type" band structure. However, the corresponding band gap is slightly decreased from 3.89 eV (polysilane)
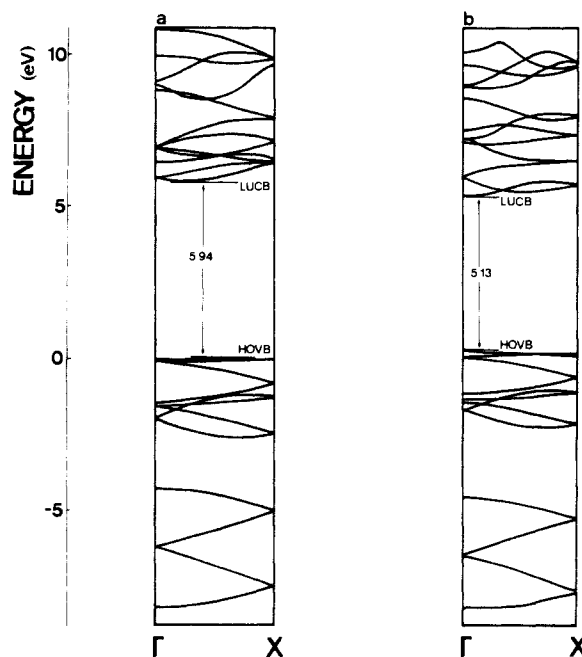
to 3.31 eV (polygermane). This decrease is qualitatively consistent with the experimental red shift in the optical absorption edge from $(SiBu_2)_n$ at 314 nm to $(GeBu_2)_n$ at 333 nm.[8]

Details of the orbital character for polysilane have already been reported in our previous papers.[26,30] They are in agreement with the other works by Bigelow[31] and also by Nelson and Pietro.[32] The orbital character for polygermane is coincident with that description; the valence band (VB) is formed of three characteristic bands of sσ, pseudo-π, and pσ bands. The highest occupied level of the valence band (HOVB) is well delocalized along the skeleton and formed of the pσ bonding state between neighboring Ge $4p_x$ orbitals. The lowest unoccupied level of the conduction band (LUCB) is the sp-hybridized state containing pσ^*-antibonding character between neighboring Ge $4p_y$ orbitals. This state is also delocalized along the skeleton.

The similarity found in the polysilane and polygermane band structures originates from an inherent similarity between Si and Ge elements. Slight differences in the polysilane and polygermane band structures tend to appear in CB's rather than in VB's; polygermane results in a larger band repulsion between two σ^* bands $(B_{3u}-B_1-A-A_1-B_{1u}$ and $B_{3u}-A_1-A-B_1-A_g)$. The LUCB state (B_{3u}) is relatively stabile in polygermane. These slight differences in CB's are basically caused by the difference in the extension of the wave functions of 3s/3p (Si) and 4s/4p (Ge).

Thus, the qualitative distinction among the group IV element skeleton polymers—polyethylene, polysilane, and polygermane— can be summed up as follows: Polyethylene has a larger band gap E_g (over the ultraviolet region ≥ 8 eV), while polygermane and polysilane have similar band gaps E_g (near the ultraviolet region 3–4 eV). Thus, polysilane and polygermane are semiconductors containing a similar wide band gap, and they apparently differ from polyethylene, which is an insulator. The relative position of the pseudo-π band is also important. Polyethylene has a pseudo-π band, which is located near the HOVB, overlaying the pσ band. On the other hand, polysilane and polygermane have a stabilized pseudo-π band that is separate from the pσ band. This means that the π-electron characteristic along the skeleton tends to be weakened from polyethylene to polysilane and polygermane.

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(27) The ideal infinite polysilane (polygermane) chain is assumed to have the following symmetry elements: (1) identity (E), (2) a mirror plane in the plane of the Si (Ge) chain (σ_{xy}), (3) mirror planes in the planes of H–Si–H (H–Ge–H) (σ_{yz}), (4) 2-fold axes bisecting H–Si–H (H–Ge–H) (C_2^y), (5) 2-fold axes bisecting Si–Si (Ge–Ge) bonds and perpendicular to σ_{xy} (C_{2x}), (6) centers of inversion at the midpoints of Si–Si (Ge–Ge) bonds (i), (7) a 2-fold screw axis lying along the chain axis (C_{2x}), (8) a glide plane containing the chain axis and perpendicular to σ_{xy} and σ_{yz} (σ_{zx}), and (9) pure translations along the chain axis. This set of symmetry elements can define its factor group. The corresponding factor group is isomorphous with the point group D_{2h}.[28] This isomorphism would allow labeling of the states according to the D_{2h} point group's irreducible representation. The factor group analysis is useful in interpreting the symmetric character of the LCAO wave functions and also the optical transitions. Therefore, classification of the chains is conventionally denoted in terms of its factor group. Note that, in the present and our previous works, the x axis is settled to the main axis of the polymer skeleton chain. This is different from the usual setting of the coordinate, in which the z axis is settled to the main axis. Therefore, one should change our $x, y,$ and z coordinates into $y, z,$ and $x,$ when referring to the usual character table.

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Table II. Band Parameters for Parent Homopolymers and Si_1Ge_1 Alternating Heterocopolymers[a]

	trans			gauche		
	Si	Si_1Ge_1	Ge	Si	Si_1Ge_1	Ge
E_g	3.89	3.84	3.31	5.94	5.67	5.13
m_e^*	0.104	0.11	0.099	1.45	0.66*	0.57
m_h^*	0.14	0.14	0.13	7.84	6.80	5.39

[a] Values of effective mass at point Γ are numerically determined by the least-squares fit from the calculated $E-k$ dispersion. Only the value of electron effective mass for GH (Si_1Ge_1), indicated by an asterisk is obtained at LUCB. All values for GH structure may be changed by more accurate fitting because of their strong localization.

3.2. Gauche-Helix Parent Polymers. According to the ab initio crystal orbital calculations,[33] the trans-planar (TP) polysilane is slightly more energetically stable than gauche-helix (GH) polysilane. However, the total energy difference between these isolated chains is only 0.15–0.38 kcal/mol per SiH_2 unit at most. This near energetic degeneracy between phases with a slightly more stable TP conformation has been previously reported by Bigelow and McGrane[34] in terms of the MNDO geometry optimizations on polysilane models. Therefore, there is a possible phase in which these two types of polysilanes are thermally mixed. The mechanism of the thermochromism is interpreted on the basis of the thermally structural phase transition from the crystalline phase of TP polysilane chains to the random phase including GH polysilane.[35] Thus, it seems to be worthwhile investigating the electronic structures of parent polymers containing the gauche-helix structure for comparison.[36] Here, we consider a typical gauche-helix with a five-pitched angle, which has four skeleton Si (Ge) atoms in a unit cell. Then, 12 occupied states will appear in the valence band.

Parts a and b of Figure 2 show the resulting band structures for *gauche*-polysilane and *gauche*-polygermane, respectively. The most significant feature, due to the change in the skeleton structure from TP to GH, is the strong localization found at the band-edge states. This is confirmed by the steep increase in the effective masses (Table II); the hole mass ratio of $m_h^*(GH)/m_h^*(TP)$ reaches about 50. Even for the LUCB state, $m_e^*(GH)$ is about 8 times larger than $m_e^*(TP)$. In the GH skeleton, skeleton atoms spiral along the skeleton direction having the direction cos $(1/\sqrt{3})$. This atomic configuration weakens the $pp\sigma$ coupling directed to the skeleton axis, roughly $1/\sqrt{3}$ smaller than that for TP skeleton, but has little influence on the $ss\sigma$ coupling because of its spherical symmetry. The orbital characters at the band edges are analogous to those for TP homopolymers; the HOVB state is a $p\sigma$ state, and the LUCB is a sp-hybridized state, including $s\sigma^*$ coupling. Therefore, the resulting HOVB state is strongly localized, but the delocalization in the LUCB state tends to be conserved. The decrease in $E-k$ dispersions at the band edges, due to the localization, opens a band gap about 1.5 times wider than that in the TP skeleton (Table II). These wider gaps in GH configuration are in agreement with the previous results by Trefonas et al.[37] and Bigelow et al.,[34] and also with our ab initio results.[33]

The formation of a GH skeleton for polysilane also moves the position of both HOVB and LUCB from point Γ to k_{HOVB} and k_{LUCB}, respectively. Since k_{HOVB} is not equal to k_{LUCB}, the resulting band actually becomes an indirect type. However, the corresponding energy differences between the band-edge states and the states at point Γ are at most 2 meV for HOVB and 91 meV for LUCB. This small difference enables the band structure
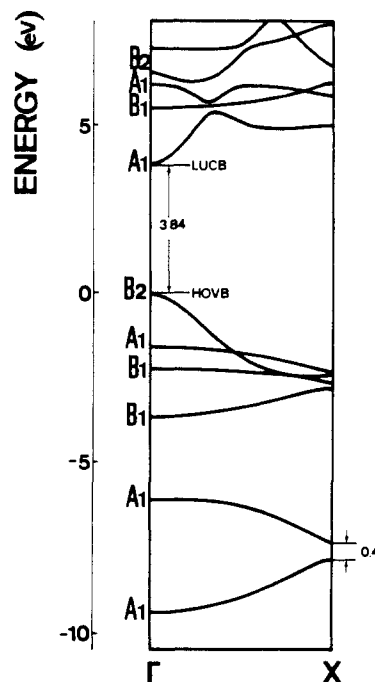

Figure 3. Electronic structure of the $(Si_1Ge_1)_n$ alternating copolymer with a transplanar zigzag form. The energy scale is represented from HOVB in electronvolts.

to appear to be equal to the direct type. On the other hand, polygermane retains the direct type structure even when the gauche-helix skeleton is formed. Consequently, the *direct type* band structure is conserved in both polysilane and polygermane, independently of the skeleton form.

Several other characteristics resulting from the change in the skeleton formed are found. The lower two bands (consisting of four $E-k$ dispersion lines) are formed mainly by σ coupling between skeleton Si 3s or Ge 4s orbitals. They correspond to the half-folded band of the $s\sigma$ band in the TP skeleton. It should also be noted that the distinct π-like states disappear in GH. Since the skeleton plane is uniquely determined in the TP structure, the orbital states, antisymmetric about this skeleton plane (π-like state), are apparently distinguished from other orbital states. On the contrary, the gauche-helix has no unique skeleton plane. This is the reason why the π-like states are not separated but are mixed with other orbitals to form an sp-hybridized state. The resulting eight states above the two $s\sigma$ bands correspond to these sp-hybridized states.

4. Si_nGe_n Ordered Heterocopolymers

4.1. Si_1Ge_1 Alternating Copolymer. Here, we consider the Si_1Ge_1 alternating copolymer, whose skeleton is formed by regular catenation of alternating Si and Ge atoms. The resulting band structure for the trans-planar Si_1Ge_1 alternating copolymer is shown in Figure 3. This alternating copolymer also shows a similar directly allowed type band structure with a 3.84-eV band gap.

The symmetry of the Si_1Ge_1 copolymer is lowered. It loses the following symmetry elements: 2-fold axes bisecting the Si–Ge bonds and perpendicular to σ_{xy} (C_2^z), centers of inversion at the midpoints of the Si–Ge bonds (i), a 2-fold screw axis lying along the chain axis (C_2^x), and a glide plane containing the chain axis and perpendicular to both σ_{xy} and σ_{yz} (σ_{zx}).[27] The resulting factor group is changed from D_{2h} (the parent homopolymers) to C_{2v}. Then, the band representations are different from those for parent homopolymers. However, the corresponding orbital characteristics are similar. The HOVB state is a $p\sigma$-bonding state between Si $3p_x$ and Ge $4p_x$ orbitals. The LUCB state is a similar sp hybridization state having $p\sigma^*$-antibonding characteristics between Si $3p_y$ and Ge $4p_y$ orbitals. These two band-edge states are also well delocalized along the skeleton. This electron delocalization in HOVB and LUCB can be also confirmed by their small ef-

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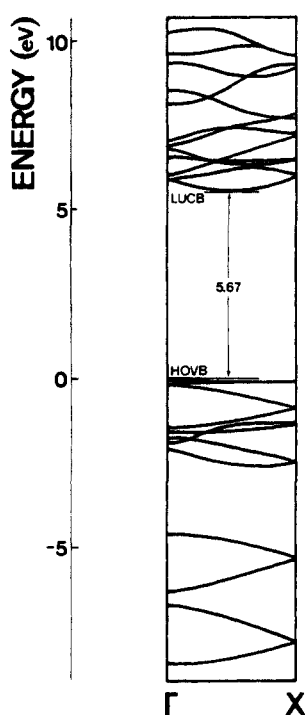
Figure 4. Electronic structure of the $(Si_1Ge_1)_n$ alternating copolymer with a gauche-helix skeleton. The energy scale is represented from HOVB in electronvolts.
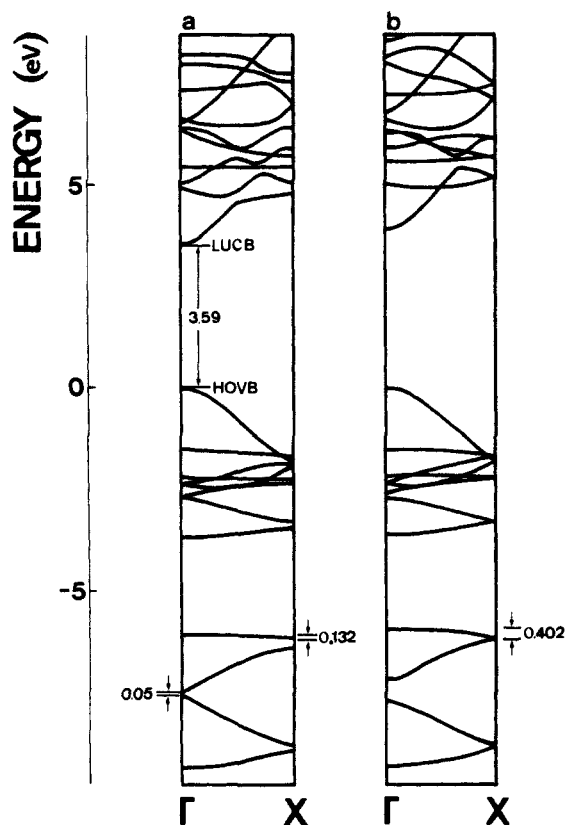

Figure 5. (a) Electronic structure of the $(Si_2Ge_2)_n$ regular copolymer. (b) Half-folded band structure of the $(Si_1Ge_1)_n$ alternating copolymer. The energy scale is represented from HOVB in electronvolts.

fective masses (Table II). The similarities found in Si_1Ge_1 copolymers and the parent homopolymers are caused by the similarity of the parent homopolymers, polysilane and polygermane.

An inherent difference from the parent homopolymer is the resolution of degenerated energy states at point X. At the zone edge (point X), one of the resolved states concentrates electrons on Si-site and the other concentrates electrons on Ge-site. In the
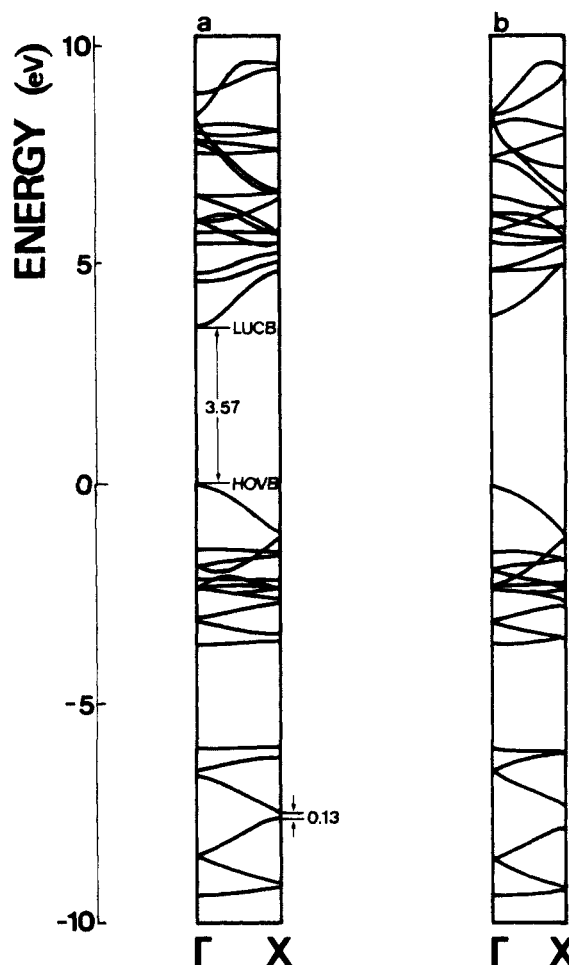

Figure 6. (a) Electronic structure of the $(Si_3Ge_3)_n$ regular copolymer. (b) Twice-folded band structure of the $(Si_1Ge_1)_n$ alternating copolymer. The energy scale is represented from HOVB in electronvolts.

parent homopolymers these two states result in the same potential energy being degenerated, because two skeleton atoms in the unit cell are homogeneous. In the Si_1Ge_1 alternating copolymer, however, this uneven distribution of electrons produces different potentials for these two states and resolves the degeneracy at point X.

The similarity of band structure between Si_1Ge_1 alternating copolymer and parent homopolymers does not disappear even when the alternating skeleton spirals into a helix form, as shown in Figure 4; the orbital characters for the $GH-Si_1Ge_1$ copolymer are same as those for the GH parent homopolymers. The band gap for $GH-Si_1Ge_1$ is also an intermediate between those of the GH parent homopolymers, similar to the TP case shown in Table II. One can then draw an analogy with the effect of copolymerization on the band structure, only if one type of the skeleton forms (TP or GH) is considered. After considering this point and our computer resources, we restricted our study of trans-planar type copolymers to the following.

4.2. Si_nGe_n Regular Copolymers. The following is a report on the electronic structures of Si_nGe_n regular (blocked) copolymers, in which Si n blocks and Ge n blocks are regularly copolymerized. Figures 5a and 6a show the resulting band structures of Si_2Ge_2 and Si_3Ge_3 regular copolymers, respectively. The band gap E_g decreases from 3.59 eV for Si_2Ge_2 to 3.57 eV for Si_3Ge_3 as n increases.

One characteristic feature of these copolymers, due to the large-block copolymerization, is the appearance of several localized levels in VB's and CB's. This localization is significant in the weak-conjugated states along the skeleton in the original Si_1Ge_1 alternating copolymer as shown in Figure 3; the strong localization can be found in the upper band of the $s\sigma$ band, whose bandwidth is decreased from 0.402 eV (the half-folded band of Si_1Ge_1 in
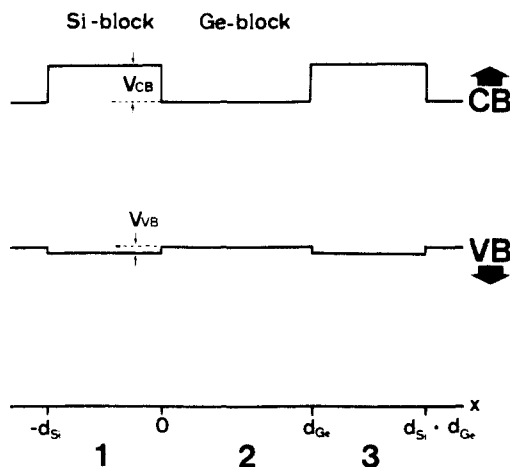
Si-block　　Ge-block

Figure 7. Illustration of potential profile at the band edges of a Ge–Si copolymer.

Figure 5b) to 0.132 eV (Si_2Ge_2). In this state, the larger block copolymerization works to sweep electrons away from the Ge block and concentrates them on the Si block. A Mulliken population analysis at point Γ shows that about 40% of the electrons in this state dissipate toward the side-group H atoms. This electron dissipation weakens the $s\sigma$ conjugation along the skeleton and enhances the uneven charge distribution among the Si block and the Ge block; the resulting charge density (CD) separation ratio, (Si block)/(Ge block), increases to 1.44, 1.72, and 3.43 as the block number n (1–3) is increased. This uneven charge distribution scissors the $s\sigma$ conjugation between the Si block and Ge block and then localizes electrons on the Si block. On the contrary, the lack of dissipation toward the side-group H atoms prevents a scissoring of the well $p\sigma$ conjugation at HOVB state. Therefore, the resulting CD separation ratio retains the value of unity. Electrons are distributed equally on both the Si block and the Ge block at the HOVB state. For this reason, the well $p\sigma$ conjugation between heterobonds of Si–Ge as well as homobonds of Si–Si or Ge–Ge hardly affects the electron delocalization at this state.

When larger regular blocks are copolymerized, band splittings at point X tend to decrease: the $s\sigma$ band for the Si_1Ge_1 alternating copolymer has a band split of 0.4 eV (Figure 3) at point X. The corresponding value is reduced to 0.05 eV (Figure 5a) for Si_2Ge_2 and to 0.13 eV (Figure 6a) for Si_3Ge_3 regular copolymers. The CD profiles for the corresponding two resolved states of Si_1Ge_1 have a peak on either the Si block or the Ge block, respectively. This type of CD profile causes a strong potential difference (see section 4.1). On the contrary, the corresponding CD profiles for the Si_2Ge_2 regular copolymer have peaks on both the Si and the Ge block, since the corresponding states are folded into point Γ. These two CD profiles have a difference only in the CD node position; one is located in the heterobonds (Si–Ge or Ge–Si) and the other located in the homobonds (Si–Si or Ge–Ge). These CD profiles weaken the potential difference, compared with that in the Si_1Ge_1 alternating copolymer. As the block number n is increased, this type of potential difference tends to become indistinguishable.

Figures 5b and 6b show the half (folded into halves, i.e., $^1/_2$) and twice (folded into thirds, i.e., $^1/_3$) zone-folded band structure of the Si_1Ge_1 alternating copolymer respectively. These folded bands agree with the calculated bands, except for several quantitative details in band resonances and band splittings at the zone edges. A second characteristic feature is that the band-edge states of these ultrathin block copolymers, even in Si_2Ge_2 and Si_3Ge_3, can be roughly estimated by the folded-band model. In ordinary two-dimensional (2D) ultrathin-layer superlattices, strong intraband and interband mixing modifies the band-edge structure.[38] Si_1Ge_1 alternating copolymer has the typical monotonous dispersion near the band edges. Therefore, zone-edge states at point

Chart I

$$\begin{vmatrix} 1 & -1 & -1 & 0 & 0 & 1 \\ -p_1 & -p_2 & p_2 & 0 & 0 & p_1 \\ 1 & 0 & 0 & -e^{ip_1(d_{Si}+d_{Ge})} & -e^{-ip_1(d_{Si}+d_{Ge})} & 1 \\ 0 & c^{ip_2d_{Ge}} & e^{-ip_2d_{Ge}} & -e^{ip_1d_{Ge}} & -e^{-ip_1d_{Ge}} & 0 \\ 0 & p_2e^{ip_2d_{Ge}} & -p_2e^{-ip_2d_{Ge}} & -p_1e^{ip_1d_{Ge}} & p_1e^{-ip_1d_{Ge}} & 0 \\ e^{ip_1d_{Si}} & 0 & 0 & -e^{ip_1d_{Ge}} & -e^{-ip_1d_{Ge}} & e^{-ip_1d_{Si}} \end{vmatrix} = 0$$

Table III. Relative CD Separation Ratio (Ge block)/(Si block) in HOVB and LUCB

Si_nGe_n	HOVB	LUCB
Si_1Ge_1	0.96	1.27
Si_2Ge_2	1.00	1.50
Si_3Ge_3	1.04	1.90

X of Si_1Ge_1 alternating copolymer, which are folded into point Γ by copolymerization, are highly energetic far from the band-edge states. Thus, little intraband mixing occurs between the band-edge states and the states folded into point Γ. Interband mixing among other folded states is inevitably excluded because of the one dimensionality (1D) of the polymer structure. For this reason, Si–Ge copolymers have a weak band-edge mixing among such folded-band states.

4.3. 1D-QW Model. Since Si_nGe_n regular copolymers have a Si–Ge periodic unit regularly, these copolymers produce a one-dimensional (1D) quantum well (QW) potential profile. The reduction in the band gap E_g, as the block number n increases, can be interpreted as the confinement effect due to a potential barrier in the QW structure.

Figure 7 shows an illustration of the modeled potential profile at the band edges. The Schrodinger equation for three regions ($j = 1$–3) is[39]

$$\frac{d^2\psi_j}{dx^2} + (p_j/\hbar)^2\psi_j = 0$$

$$p_j^2 = 2m_j^*(\epsilon - V_j) \tag{2}$$

where ϵ is the requantized energy eigenvalue to be solved and V_j is the simplified potential energy in the region j. The generalized solution for this equation is

$$\psi_j = A_j^+ e^{i(p_j/\hbar)x} + A_j^- e^{-i(p_j/\hbar)x} \tag{3}$$

The boundary condition at $x = 0$ and $x = d_{Ge}$ gives

$$\psi_1(0) = \psi_2(0)$$
$$\dot{\psi}_1(0) = \dot{\psi}_2(0)$$
$$\psi_2(d_{Ge}) = \psi_3(d_{Ge})$$
$$\dot{\psi}_2(d_{Ge}) = \dot{\psi}_3(d_{Ge})$$
$$\psi_1(-d_{Si}) = \psi_3(d_{Ge})$$
$$\psi_1(0) = \psi_3(d_{Si} + d_{Ge}) \tag{4}$$

Therefore, the requantized energy eigenvalue ϵ can be obtained by solving the 6 × 6 secular matrix in Chart I. In Chart I, the relation $p_1 = p_3$ and the atomic unit of $\hbar = 1$ and $m_0 = ^1/_2$ are used.

When the Si and Ge blocks grow, the reflection waves from these blocks can be negligible. In this situation ($A_1^+ = A_3^- = 0$), the following simplest solution (model I) can be derived by solving the upper 4 × 4 determinant of Chart I:

$$\tan [\hbar^{-1}(2m_j^*\epsilon)^{1/2}d_{Ge}] = \frac{2[\epsilon(V_j - \epsilon)]^{1/2}}{2\epsilon - V_j} \tag{5}$$

On the contrary, the ultrathin blocked copolymer has shorter block lengths, and then one should take into account the reflection waves

(38) Nakayama, T.; Kamimura, H. *J. Phys. Soc. Jpn.* **1985,** *54,* 4726. Nakayama, T. Ph.D. Thesis, University of Tokyo, 1987.

(39) Schiff, L. I. *Quantum mechanics,* 3rd ed.; McGraw-Hill: New York, 1968; p 37.
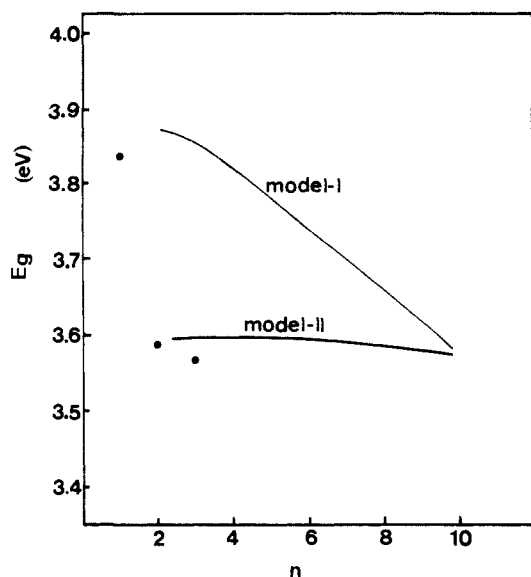
Figure 8. Energy band gaps of a Si_nGe_n regular copolymer ($n \leq 3$). Calculated values by models I and II are also given.

Figure 9. $E-k^2$ dispersion curves near the band edges of HOVB and LUCB.

and exactly solve the above 6 × 6 secular equation (model II). Here, the requantization of the band-edge states was investigated by the two models above.

Values of band offsets for the CB and VB edges were estimated as follows. Table III shows the CD separation ratio between the Si block and Ge block for the HOVB or LUCB state of Si_nGe_n ($n \leq 3$) copolymers, respectively. While the HOVB state conserves electrons to be distinguished equally between Si blocks and Ge blocks with increasing n values, electrons in the LUCB state concentrate in the Ge block with increasing n number. This means that most of the band discontinuity occurs at the CB edge, not at the VB edge. Therefore, it seems a reasonable assumption that the CB band offset is approximately equal to the energy difference between the polysilane and polygermane band gaps ($\Delta E_g = 0.58$ eV). Values for the effective masses m_j^* for CB and VB are summarized in Table II.

Since model I neglects the influence of reflection wave from neighboring Si barrier blocks, the effect of the requantization in QW is overestimated (Figure 8). Therefore, it results in an inconsistently large band gap, particularly in the ultrathin block ($n = 3-6$) region. This overestimation decreases as the block number ($n \geq 8$) increases. Values of the band gap are significantly improved by taking into account the influence of reflection from the neighboring barriers (model II). The resulting values agree well with those derived by using the LDF band calculation, even in the ultrathin block region. In order to obtain quantitatively more consistent values, one should take into account the interaction from the second, third, and higher blocks, as well as more accurately estimating the band offsets.

To which copolymers can the effective mass theory (e.g., Kronig-Penny model) be adapted? In the Kronig-Penny model, the band offsets between heteroblocks should be included. However, it neglects the nonparabolicity in $E-k$ dispersion because of its effective mass approximation. Figure 9 shows the $E-k^2$ plots for the VB and CB edges near point Γ. The points indicated by the arrows, where nonparabolicity begins to appear, corresponds to the zone edge of about 5 times folded Brillouin zone. This means that, for Si-Ge copolymers having over five blocks, the band-gap electronic structure can be approximately estimated by using the effective mass theory, and one can image a picture of a 1D-QW wire model.

5. Si_mGe_n Ordered Heterocopolymers

5.1. Si_mGe_n Blocked Copolymers. Here, we discuss the electronic structure of Si_mGe_n ($m \neq n$) blocked copolymers, in which Si m atoms and Ge n atoms are catenated in order. Table IV shows the blocked copolymers, Si_mGe_n ($m + n \leq 6$), considered in this work.[40] Figures 10-12 show the corresponding band
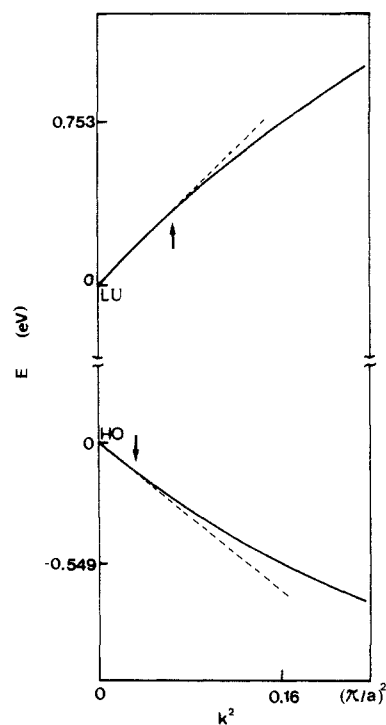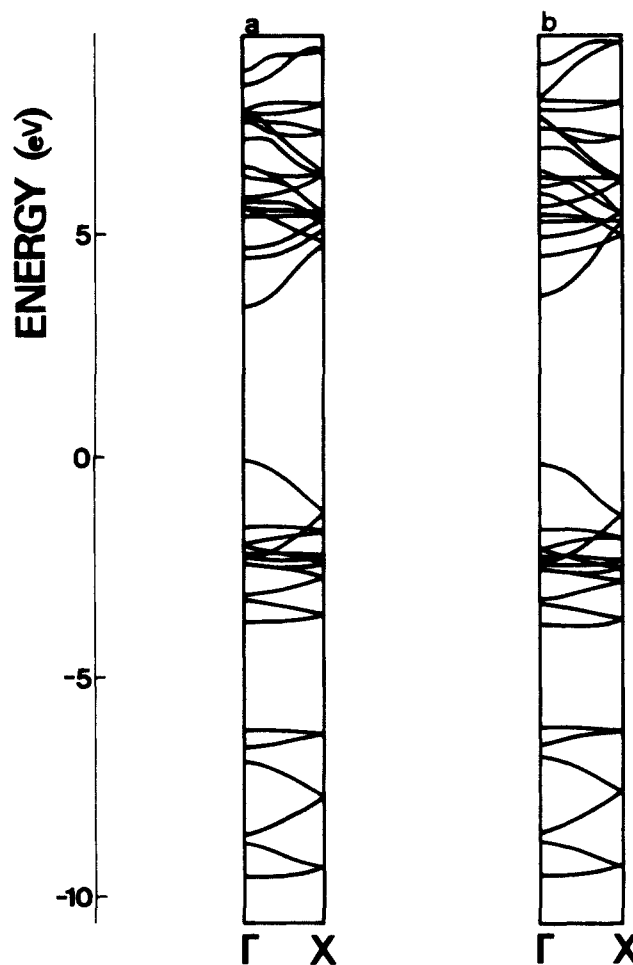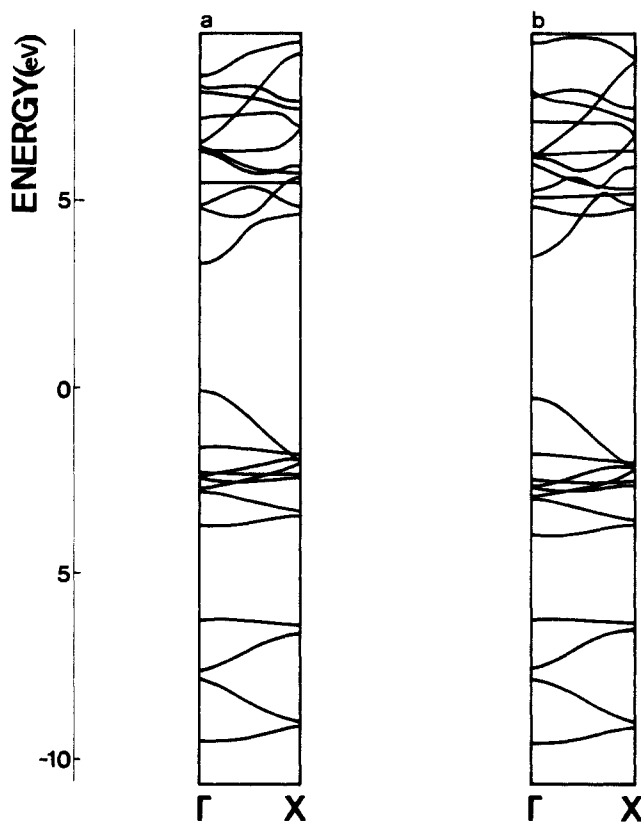

Figure 10. Electronic structures of Si_mGe_n blocked copolymers for the $m + n = 3$ system: (a) Si_1Ge_2; (b) Si_2Ge_1. The energy scale is represented from HOVB in electronvolts.

structure for Si_mGe_n blocked copolymers of the $m + n = 3$, 4, and 6 systems, respectively. The characteristics of these band

Table IV. Classification of Several Si_mGe_n Copolymers

$m + n$	m	n	factor group	Ge ratio
2	1	1	C_{2v}	0.5
3	1	2	D_{2h}	0.666
	2	1	D_{2h}	0.333
4	1	3	C_{2v}	0.75
	2	2	C_{2h}	0.5
	3	1	C_{2v}	0.25
5	1	4	D_{2h}	0.8
	2	3	D_{2h}	0.6
	3	2	D_{2h}	0.4
	4	1	D_{2h}	0.2
6	1	5	C_{2v}	0.833
	2	4	C_{2h}	0.666
	3	3	C_{2v}	0.5
	4	2	C_{2h}	0.333
	5	1	C_{2v}	0.166

Figure 11. Electronic structures of Si_mGe_n blocked copolymers for the $m + n = 4$ system: (a) Si_1Ge_3; (b) Si_3Ge_1. The energy scale is represented from HOVB in electronvolts.

structures can be fundamentally interpreted by the corresponding zone-folded band structure of the Si_1Ge_1 alternating copolymer, to be similar to the case of Si_nGe_n regular copolymers. The reason is that the similarities in polysilane and polygermane produce small band offsets.

$m + n = 3$ System. The factor group of blocked copolymers in this system is isomorphic to the point group D_{2h}. The unit cell includes two primitive Si_mGe_n units due to the trans-planar zigzag structure of the skeleton. Therefore, the number of Si and Ge atoms in the $m + n = 3$ system is same as that in the $m + n = 6$ system, and the unit cell of Si_1Ge_2 or Si_2Ge_1 blocked copolymers is analogous to that of Si_2Ge_4 or Si_4Ge_2 copolymers of the $m + n = 6$ system, respectively. For this reason, the resulting band structures (Figure 10) are similar to those of the $m + n = 6$ system (Figure 12b,c), as well as that of twice-zone-folded band structure (Figure 6b). However, there is an inherent difference from the $m + n = 6$ system; the symmetry[27] of the $m + n = 3$ system does

not allows the band splitting at point X but retains its energy degeneracy.

$m + n = 4$ System. Although the factor group of Si_2Ge_2 regular copolymer is isomorphic to the point group C_{2h}, those of the other blocked copolymers (Si_1Ge_3 and Si_3Ge_1) are to the point group C_{2v}. This symmetry difference, however, causes little difference in the band structure as shown in Figure 11. The significant feature due to the blocked copolymerization is the localization of the pseudo-π and pseudo-π^* band states. The localization of the pseudo-π^* states is particularly significant over the $m + n \geq 4$ systems.

$m + n = 6$ System. In this system, copolymers with odd m and odd n composition numbers have the factor group isomorphic to the point group C_{2v}, and those with even m and even n composition numbers have that to the point group C_{2h}. The difference in symmetry has a slight influence on the band splits folded into point X (Figure 12); the latter copolymers (Si_2Ge_4 or Si_4Ge_2) tend to cause smaller band splitting compared with the former copolymers (Si_1Ge_5 or Si_5Ge_1). As discussed in the $m + n = 3$ system, the latter copolymers are similar to copolymers in the $m + n = 3$ system, having no band splittings, in the points of their unit cells as well as their reduced composition ratios. This similarity is the reason why the band splittings in the latter copolymers (Si_2Ge_4 and Si_4Ge_2) are smaller than those in the former copolymers (Si_1Ge_5 and Si_5Ge_1).

5.2 Energy Band Gaps. Here, we focus on the values of the energy band gaps E_g for Si_mGe_n blocked copolymers. Figure 13 shows the calculated E_g values for the blocked copolymers summarized in Table IV. Blocked copolymers, even with the same Si/Ge composition ratio, give different band gap values depending on their Si–Ge ordering length: blocked copolymers including larger Ge blocks result in smaller band gaps (compared with Si_1Ge_1, Si_2Ge_2, and Si_3Ge_3, or with Si_1Ge_2 and Si_2Ge_4, or with Si_2Ge_1 and Si_4Ge_2). This is because the band gap values approach that of polygermane with increasing Ge block, since electrons tend to localize in the lower potential block (i.e., Ge block plays a role of a "electron pocket" at the band-edge states in Si–Ge copolymers).

Band gaps both for Ge monoblock and Si monoblock copolymers also decrease with an increasing Ge ratio in the polymer. However, the E_g decrease found in Ge monoblock copolymers does not coincide with, but is smaller than, that in Si monoblock copolymers. Then, the E_g value for Si_1Ge_1 alternating copolymer, as estimated by the extrapolation from Si monoblock copolymer (3.68 eV), does not coincide with that derived by the extrapolation from Ge monoblock copolymer (3.75 eV). Moreover, the resulting $E_g(Si_1Ge_1)$ value derived by the LDF band calculation has a larger value (3.84 eV) than both of the above estimated values. This type of discontinuity is the most characteristics feature in Si_1Ge_1 alternating copolymer (i.e., *1D ultrathin blocked superlattice high polymer*).

E_g values for disordered and/or random copolymers Si_xGe_y are qualitatively estimated. In a random copolymer Si_xGe_y, only the total composition ratio of Si/Ge $= x/y$ is seemingly determined. This type of copolymer can be called an alloyed polymer rather than a superlattice polymer. Since Si and Ge atoms are randomly catenated, a straightforward application of the band calculation is not possible. Here, E_g values for such random copolymers are estimated with a virtual polymer model.

Based on the fact that the Si–Ge mixed-alloy compound system shows a good Vegard's law in its lattice constants,[41] the alloying effect is taken into account through the change in bond length by using the compositionally averaged bond length. Fluctuation in E_g values caused by the random disordering of Si and Ge atoms is estimated by using the following two types of the limited virtual polymers: One of them is virtual polysilane, in which all potentials for virtual atoms are replaced by the Si atom potential. The other is a virtual polygermane, whose potential is replaced by the Ge atom potential. Actual random or disordered copolymers Si_xGe_y would have a potential among those of above two limited virtual

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(40) The $m + n = 5$ system has not been performed in this work yet because of the rack in the available computer's memory.

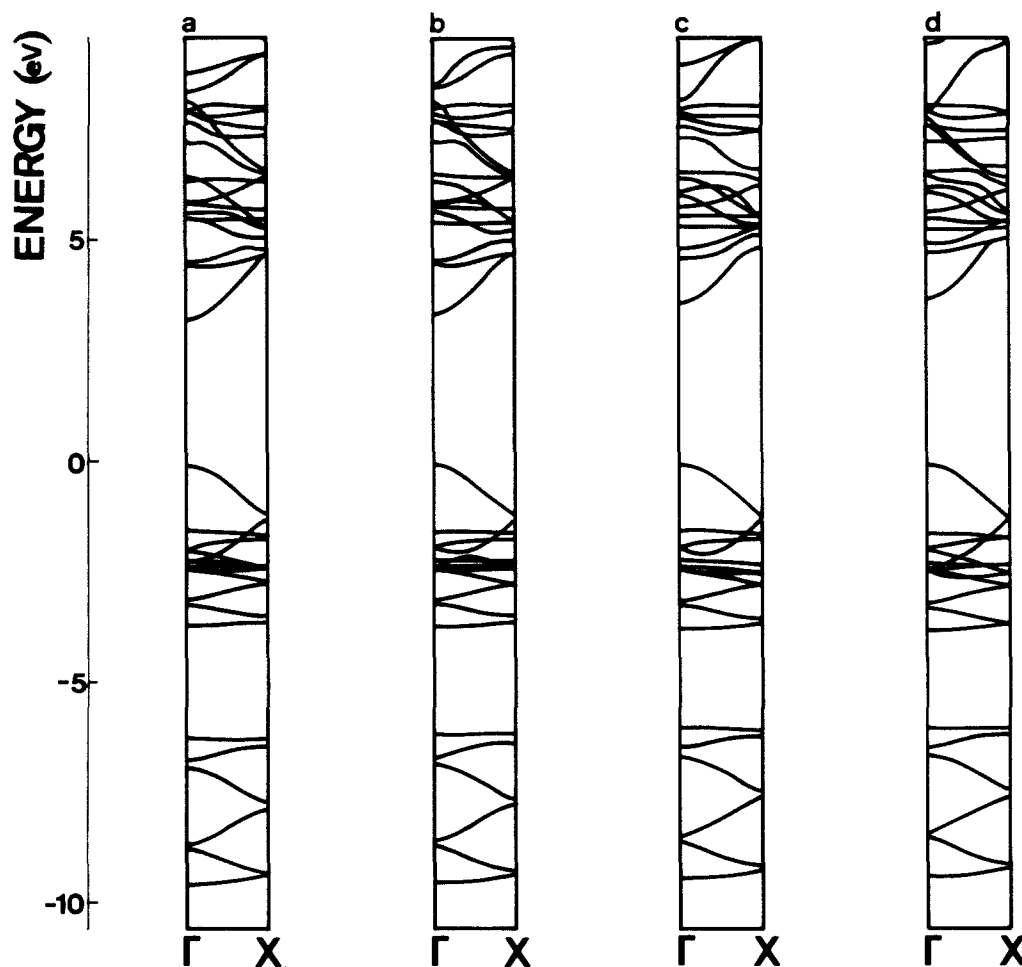(41) Johnson, E. R.; Christian, S. M. *Phys. Rev.* **1954**, *95*, 560.

Figure 12. Electronic structures of Si_mGe_n blocked copolymers for the $m + n = 6$ system: (a) Si_1Ge_5; (b) Si_2Ge_4; (c) Si_4Ge_2; (d) Si_5Ge_1. The energy scale is represented from HOVB in electronvolts.
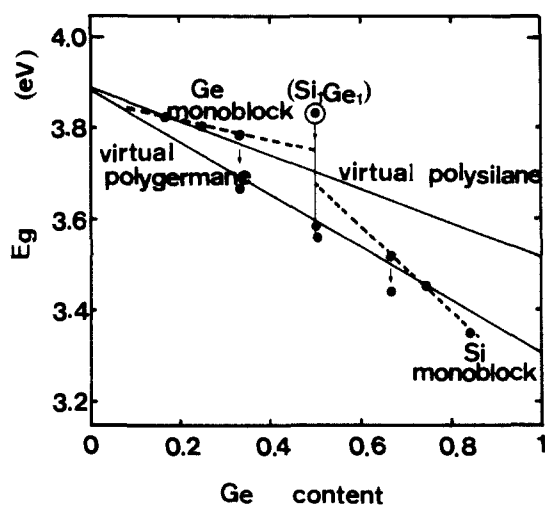

Figure 13. Band gaps for Si_mGe_n blocked copolymers and Si_xGe_y disordered copolymers.

polymers. After LDF bands were calculated for these two types of virtual copolymers with varying a composition ratio, we determine virtual E_g values.

The calculated E_g values for both virtual polysilane and virtual polygermane agree well with Vegard's law as shown in Figure 13. This is because of the *gentleness* of the Si and Ge elements.[42] The actual E_g values for random copolymers Si_xGe_y are expected to

be in the screened region surrounded by these limited virtual values (disordered region). The fluctuation in E_g values increases when the Ge ratio increases. This is consistent with the behavior of Ge-rich Si_xGe_y random copolymers, i.e., an increase in the possibility of producing many kinds of Ge blocks having different Ge block lengths, which cause several types of requantized band-edge states to magnify the fluctuation of E_g values.

The E_g values for ordered copolymers should be compared with those for disordered copolymers. In the Si-rich region (Si/Ge > 1), the E_g values for Ge monoblock ordered copolymers are larger than those for disordered copolymers. The growth of larger Ge blocks (e.g., Ge double-block copolymers) decreases their E_g values and allows the values to fall outside the corresponding disordered region, because the E_g fluctuation of the random copolymers is narrow in this region (Si/Ge > 1). In the Ge-rich region (Ge/Si > 1), Si monoblock ordered copolymers originally have smaller E_g values compared with those for disordered copolymers. Therefore, the resulting E_g values for ordered copolymers are similarly outside the disordered region, in spite of the fact that random copolymers in this region have a wide range of E_g values. Thus, Si_mGe_n ordered copolymers might be expected to appear out of the disordered region to give E_g values different from those for Si_xGe_y disordered copolymers, even if their composition ratios are same $(m/n = x/y)$.

5.3. Optical Transition. Finally, the influence of Si–Ge ordered copolymerization on the optical transition profile from HOVB level is investigated. For the finite polysilane oligomers, the MNDO analysis on the optical transition matrix (OTM) element has been previously performed by Bigelow and McGrane.[34] The absorption coefficients for the infinite polysilane chains have been theoretically investigated by Mintmire[44] in terms of the LDF

(42) Takeda, K.; Taguchi, A.; Sakata, M. *J. Phys. C: Solid State Phys.* **1983**, *16*, 2237.

(43) In a trans-planar skeleton, Si_1Ge_2 and Si_2Ge_4 have the same number of Si and Ge atoms in the unit cell.

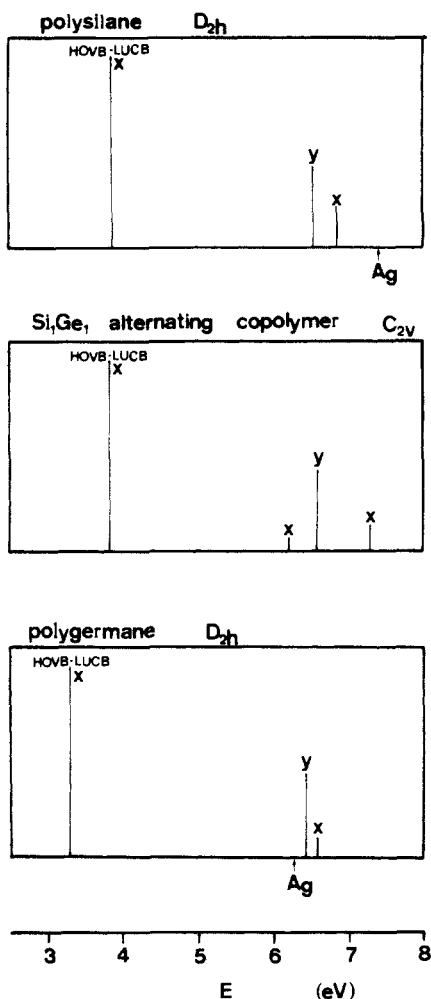(44) Mintmire, J. W. *Phys. Rev.* **1989**, *B39*, 1350.

Figure 14. Optical transition profile for polysilane (a), $(Si_1Ge_1)_n$ alternating copolymer (b), and polygermane (c). OTM values are normalized by the HOVB–LUCB transition. Symbols x, y, and z indicate the direction of polarization of the excitation light. The skeleton chain of polymers is configured in the x–y plane. The corresponding factor group is also shown in figure.

Figure 15. Optical transition profile for the $m + n = 4$ system of $(Si_1-Ge_3)_n$ (a), $(Si_2Ge_2)_n$ (b), and $(Si_3Ge_1)_n$ blocked copolymer (c). OTM values are normalized by the HOVB–LUCB transition. Symbols x, y, and z indicate the direction of polarization of the excitation light. The skeleton chain of polymers is configured in the x–y plane. The corresponding factor group is also shown in figure.

calculation. Since the ordered copolymerization changes the symmetrical property of copolymers, the OTM term in the absorption coefficient should be discussed in this section.

The OTM term, $M_{\mu\nu}(k)$, from the $|\Psi_k^\mu\rangle$ state in μth band to the $|\Psi_k^\nu\rangle$ state in νth band is defined as

$$M_{\mu\nu}(k) \sim \langle \Psi_k^\nu(r)|\nabla|\Psi_k^\mu(r)\rangle \tag{6}$$

The wave function $|\Psi_k^j\rangle$ can be expressed by the plane wave expansion as

$$\Psi_k^j(r) = \sum_g \alpha_{k-g}^j e^{i(k-g)r} \tag{7}$$

Therefore, the OTM $M_{\mu\nu}(k)$ is rewritten as

$$M_{\mu\nu}(k) \sim \sum_g (k - g)\alpha_{k-g}^{\nu*}\alpha_{k-g}^\mu \tag{8}$$

Since the LDF band calculation numerically gives the wave function $\Psi_k^j(r)$, the expansion coefficient α_{k-g}^j is first obtained by fast Fourier transformation and then the value of $M_{\mu\nu}(k)$ is calculated.

The OTM value gives a maximum for the transition from HOVB to LUCB and then decreases with increasing energy (Figure 14). In parent homopolymers whose factor group is isomorphous with the point group D_{2h} (polysilane and polygermane), optical transitions from HOVB to the A_g level (σ-like state) as well as the B_{2u} level (π-like state) in CB's are forbidden. Therefore, only three possible absorption peaks appear in the energy region between 3 and 7.5 eV. The lowering of the symmetry, due to alternating copolymerization, changes the A_g orbital
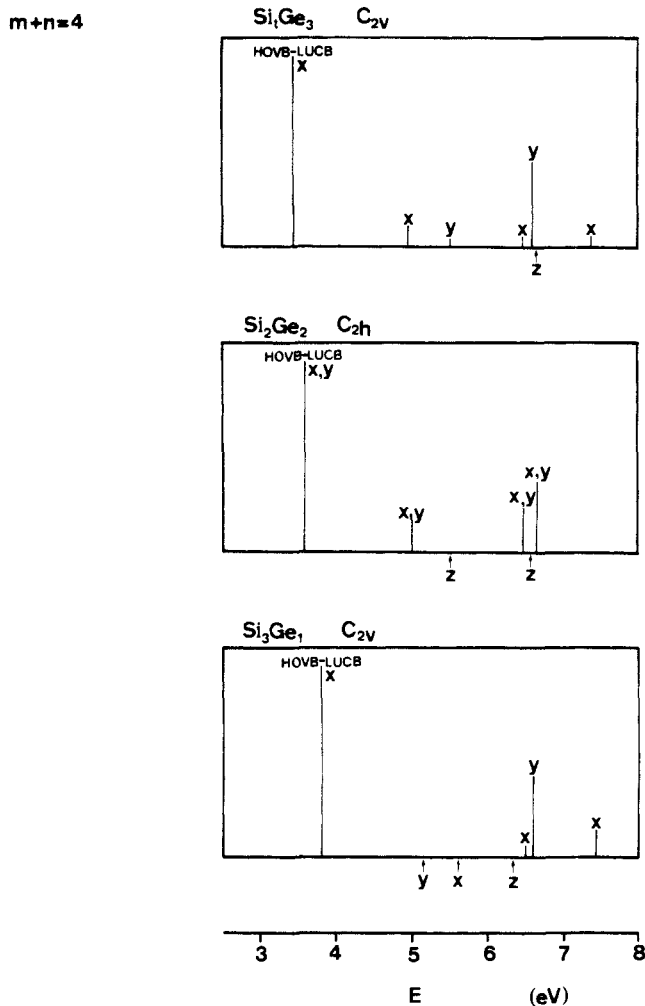
symmetry into the A_1 orbital symmetry, into which optical transition from HOVB (B_2) is allowed. Four absorption peaks might in principle be found in the same energy region except that their calculated OTM values are very small.

The ordered regular ($m = n$) and/or block ($m \neq n$) copolymerization introduces the zone-folding image in the copolymer band structures. Due to this copolymerization, new states folded from point X are formed at point Γ. Thus, it becomes possible that new optical transition processes occur from HOVB to these newly formed states. The resulting OTM for the $m + n = 4$ system is shown in Figure 15. The figure shows that Si_2Ge_2 has four peaks, while Si_1Ge_3 or Si_3Ge_1 has six peaks. The copolymerization increases the number of OTM peaks in the 3–7.5-eV energy region. The difference in symmetry also produces a different optical transition profile.

The Si–Ge heteroatom copolymerization causes one more important feature in the OTM profile. That feature is that copolymers having a different ordering length of homoatoms give different OTM values, even if they have the same factor group symmetry. For example, the Si_3Ge_1 copolymer gives smaller OTM values, which cannot be observed clearly, compared with those values for the Si_1Ge_3 copolymer, in spite of their same factor groups (C_{2v}). As discussed in the previous section, the band offset between Si block and Ge block is indistinct at the HOVB state. Since the copolymers in the $m + n = 4$ system have four skeleton atoms in the unit cell, one-fourth of the electrons are, then, distributed to each of the skeleton atoms at this state, independently of the kind of atoms of Si and Ge. This is true for both Si_1Ge_3
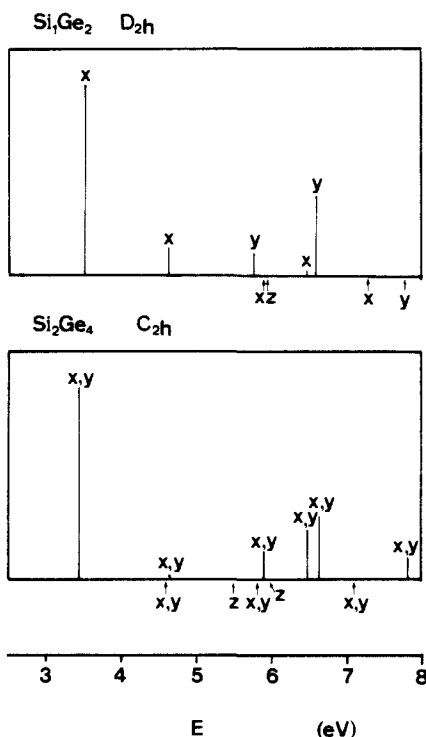
Si₁Ge₂   D₂h

Si₂Ge₄   C₂h

Figure 16. Optical transition profile for copolymers having same Si–Ge composition ratio: Si₁Ge₂ (a); Si₂Ge₄ (b). OTM values are normalized by the HOVB–LUCB transition. Symbols x, y, and z indicate the direction of polarization of the excitation light. The skeleton chain of polymers is configured in the x–y plane. The corresponding factor group is also shown in figure.

and Si_3Ge_1 copolymers. However, the corresponding band offsets in CB's are significant so as to concentrate electrons strongly in Ge block. Since the Si_3Ge_1 copolymer has only one Ge block in the unit cell, electrons tend to be confined in a smaller region than in the Si_3Ge_3 copolymer. This spatial confinement reduces the overlap of the wave functions between the initial (HOVB) and the final state and then results in the small OTM values found in the Si_3Ge_1 copolymer. On the contrary, the weak spatial separation between the HOVB and the CB's wave function lets Si_1Ge_3 copolymer be an optically active QW wire.

When copolymers have an equal Si–Ge reduced composition ratio, they show analogous OTM values (Figure 16) except for their OTM profiles. Since copolymers with the same composition ratio have an equal Ge block length entirely within the unit cell,[43]

the spatial confinement of the wave function in CB's roughly coincides. This type of the coincidence preserves the value of the wave function overlapping between the initial (HOVB) and the final states equally among these copolymers. This is the reason why copolymers with the same composition ratio cause similar OTM values. Thus, for Si–Ge copolymers, the length of the Ge block, i.e., the electron pocket length, plays an important role in the OTM profile.

6. Conclusions

1. Polysilane and polygermane having a TP skeleton have a direct band gap of 3.89 and 3.31 eV, respectively. On the contrary, those having a GH skeleton have about 1.5 times larger values: 5.94 eV for GH polysilane and 5.13 eV for GH polygermane. However, the direct-type band structure is conserved independently of the skeleton forms of TP and GH.

2. TP Si_1Ge_1 alternating copolymer also has a direct band gap of 3.84 eV. The alternating copolymerization resolves the energy degeneracy at point X.

3. The ordered regular and/or block Si–Ge copolymerization introduces the zone-folding image in the copolymer band structures. Si_mGe_n ordered copolymers have the potential to be the 1D superlattice high polymers.

4. For Si–Ge copolymers having over five blocks, the band-edge electronic structure can be approximately estimated by using the effective mass theory and a picture of a 1D-QW wire model can be imaged.

5. Ge block plays the role of a electron pocket for HOVB and LUCB states in Si–Ge copolymers.

6. Si_mGe_n ordered copolymers might be expected to have E_g values different from those for Si_xGe_y disordered copolymers, even if their composition ratios are the same ($m/n = x/y$).

7. The ordered (regular and/or block) copolymerization introduces new states at point Γ, which are folded from point X. New optical transition processes occur from HOVB to these newly formed states. This increases the number of possible OTM peaks as well as changes the OTM profile.

Automerization of Cyclobutadiene

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Contribution from the Department of Chemistry, Technion—Institute of Technology, Haifa 3200, Israel. Received June 12, 1989

Abstract: Two ways of calculating the tunneling rate for the automerization of cyclobutadiene are examined. One is based on an energy splitting and the other on a transmission probability. It is argued that the latter procedure is the appropriate one for a treatment of automerization in the condensed phase.

1. Introduction

Automerization of cyclobutadiene is usually considered to be an example of tunneling involving heavy atom motion. This suggestion was originally made by Carpenter,[1] following experiments by Whitman and Carpenter[2] with two differently deu-

terated cyclobutadienes as reaction intermediates. Carpenter[1] made an estimate of the tunneling rate by multiplying the frequency of the promoting mode for automerization (essentially the antisymmetric C–C stretch) by the transmission probability (TP)

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(1) Carpenter, B. K. J. Am. Chem. Soc. 1983, 105, 1701.
(2) Whitman, D. W.; Carpenter, B. K. J. Am. Chem. Soc. 1980, 102, 4272.