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Electronic Structure of Poly(dimethylsilane) and Polysilane Studied by XPS, UPS, and Band Calculation

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The valence electronic structures of poly(dimethylsilane)(PDMS) $(Si(CH_3)_2)_n$ and polysilane $(SiH_2)_n$ were studied. PDMS was experimentally studied by X-ray photoelectron spectroscopy (XPS) and UV photoelectron spectroscopy (UPS), and band calculations were performed for both compounds. The observed spectral features and calculated band structures were assigned and discussed through a comparison with theoretical and experimental results for oligomers and other polymers. These analyses have demonstrated how the electronic structures of these compounds are correlated through factors such as (i) change in the chain length, (ii) methylation, and (iii) the substitution of Si by C. PDMS has a small ionization energy (5.9 eV) almost as low as that of poly(*p*-phenylene) (5.6 eV). This small value comes from the combined contribution from the small electronegativity of silicon, σ-conjugation, and the inductive effect of methyl groups. The small ionization energy and large σ-conjugation explain the reported high conductivity of PDMS and its derivatives upon acceptor doping.

Recently the electronic properties of polysilane $(SiH_2)_n$ and their derivatives have attracted considerable interest from various viewpoints such as the strong delocalization of σ-electrons (σ-conjugation),[1-3] a new class of conducting polymers,[1,4,5] photoresists,[1] photoinitiators for polymerization,[1] and species found in the films of plasma-deposited Si:H alloy.[6,7] The permethylated or other organo-substituted compounds are used for protecting the polysilane backbone from unstability to air.

The elucidation of the electronic structures of polysilane and poly(dimethylsilane) $(SiMe_2)_m$ (PDMS), which is the simplest poly(organosilane), is the basis for such studies. However, the electronic structures of these compounds have not been investigated experimentally, although shorter members of silanes Si_nH_{2n+2} $(n\leqslant 5)$[8,9] and permethylated silanes $Si_m(CH_3)_{2m+2}$ $(m\leqslant 5)$[8,10] have been extensively studied by gas phase UV photoelectron spectroscopy (UPS). On the theoretical side, there have been several band calculations for polysilane and their derivatives.[11-13] A recently reported UPS study of polysilanes with complex pendants[14] clarified several important points such as the dominant contribution of the large pendants to their electronic structure and the relation of chain-pendant interaction with their ability as photoresists. Unfortunately, however, the topmost part of the valence band could not be studied in detail, and there is a large uncertainty in the energy axis due to sample charging.

In this paper we report on a study of the whole valence electronic structures of PDMS and polysilane. PDMS is studied by X-ray photoelectron spectroscopy (XPS) and UPS. Such experiments could not be performed on unstable unsubstituted polysilane, but band calculations were performed on both compounds; the results are discussed in terms of the relevant data for oligomers. A comparison is also made with polyethylene $(CH_2)_n$, the carbon analogue of polysilane, and conducting polymers with π-conjugated carbon chains.

Furthermore, in the process of sample preparation we found that thin films of PDMS can be prepared by vacuum-evaporation, a technique which has been successfully applied to other polymers such as polyethylene and polypropylene.[15] This technique may also be applicable for the thin-film preparation of other polysilanes.

Experimental

The PDMS powder was supplied from Shinnisso-Kako Co. Ltd., and used without further purification. The XPS spectra were measured on a VG ESCALAB 5 photoelectron spectrometer using Al *K*α radiation ($h\nu$=1486.6 eV). The sample powder was supported on a Nichiban double-sided adhesive tape.

The UPS spectra were measured using two photoelectron spectrometers with different light sources, i.e. (i) rare-gas resonance lines (He I, $h\nu$=21.2 eV; Ne I, $h\nu$=16.8 eV, and Ar I, $h\nu$=11.7 eV), and (ii) the combination of a Hinteregger-type hydrogen discharge lamp with a 0.5-m Seya-Namioka-type monochromator ($h\nu$=7.7—10.5 eV). The base pressure of the chamber was ca. 5×10^{-8} Pa and ca. 2×10^{-4} Pa for spectrometers (i) and (ii), respectively. In both cases, the energy analyzer of photoelectrons was a retarding-potential type one. The photoelectron spectra were obtained using an ac moduation technique,[16,17] with a modulation of 0.2 V peak to peak.

One advantage of the retarding-potential-type analyzer is that we could accurately determine the absolute binding energy.[16,17] In order to use this advantage for insulators, however, a thin film of several tens nm thickness was necessary for avoiding sample charging. Such a film was obtained by in-situ vacuum-evaporation in the photoelectron spectrometer to a thickness of 25 nm, which was monitored by a quartz oscillator.

The evaporated film was examined by IR spectroscopy.

The IR spectrum of PDMS before evaporation was measured with a KBr pellet, and agreed well with the reported spectrum.[18] It exhibits bands due to adsorbed water at 3440 cm^{-1} and 1650 cm^{-1}, and a band due to Si–O bond at 1035 cm^{-1}. We also observed a weak oxygen ls peak in the XPS spectrum of the powder, which corresponds to a few per cent of O atom per Si atom. Such a small amount of oxygen is not expected to affect the observed UPS and valence-XPS spectra. A weak band due to the Si–H stretching also appears at 2100 cm^{-1}. In the spectrum of a film evaporated onto a KBr disk, water-derived bands are completely removed and the Si–O band becomes weak. On the other hand, the Si–H band becomes stronger, and the band around 700 cm^{-1}, which is related to the Si–C bonds, becomes weaker. From these results, we conclude that some of the CH_3 groups are replaced by H atoms upon evaporation: however, main structure of PDMS is preserved.

The evaporated film did not sublime away, even after a long storage in high vacuum. This indicates that the molecular weight of PDMS in the evaporated film is much larger than those of the short oligomers ($n \leqslant 5$) studied in gas-phase UPS experiments.[8,10]

Calculation

The band structure calculations were performed with an extended Hückel approximation using a program described elsewhere.[19] Parameters by Nguyen et al.[20] (Table 1) were used.

The validity of this method was examined by comparing the observed gas phase UPS spectra of small silanes[8] and methylated silanes[10] with the calculated energy levels by this method without Si 3d orbitals. The calculated results compare reasonably well with the observed UPS spectra, when we shift the calculated results by about 2 eV to the lower-energy side. The character of calculated levels also agree well with the experimentally assigned ones by Bock et al.[8–10] These results indicate that we can use this rather primitive method for discussing the gross features of the electronic structures of polysilane and PDMS.

We also calculated the molecular orbitals of Si_2H_6 with (i) the use of a slightly smaller orbital exponent $\zeta=1.2$ for Si and (ii) an extended basis set including the Si 3d orbital. The results showed that these changes have little effect on the calculated results. Since the calculated band structures of PDMS and polysilane are also little affected by these changes, we report here only the results without 3d orbitals and $\zeta=1.383$.

Band structure calculations of polymers were performed for polysilane, PDMS, and polyethylene. All three polymers were taken to be in a planar-zigzag conformation: The bond angles and bond lengths are listed in Table 1(b). This conformation has not yet been experimentally verified for polysilane and PDMS, and other possibilities are also suggested.[23] However, UPS and XPS experiments on crystalline and gaseous alkanes[24] indicate only a minor difference of the density-of-states between extended planar-zigzag and random-coil conformations. Therefore, the results for an adopted conformation will be at least a good first-

Table 1. Parameters for Band Calculations.
(a) Extended Hückel Parameters[20]

	$-H_{ii}$/eV	Exponent ζ
H ls	13.60	1.000
C 2s	21.40	1.625
C 2p	11.40	
Si 3s	17.31	1.383
Si 3p	9.20	
Si 3d	6.00	

(b) Bond Lengths (in pm) and Bond Angles (in Degrees)

Si-Si	226.4[a]
Si-C	186.7[b]
C-C	152.93[c]
Si-H	149.3 (polyethylene)[a]
C-H	106.89 (polyethylene)[c]
	112.7 (PDMS)[b]
<SiSiSi	118.97[a]
<CSiC	110.5[b]
<HSiH	100.39[a]
<HCH	110.3 (PDMS)[b]
	107.0 (polyethylene)[c]
<CCC	112.0[c]

a) From the optimized geometry in Ref. 12. b) From the molecular structure of hexadimethylsilane.[21] c) From the X-ray geometry cited in Ref. 22.

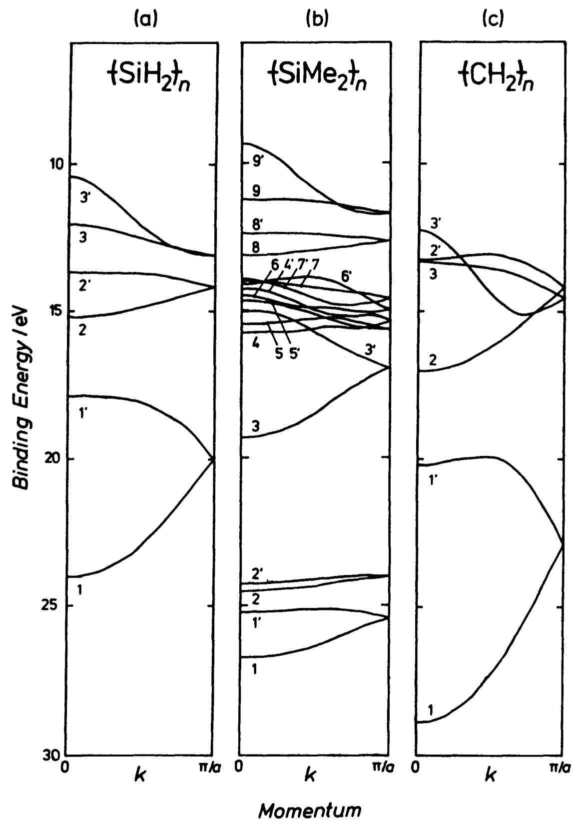

Fig. 1. Calculated enegy band structures of (a) polysilane, (b) poly(dimethylsilane), and (c) polyethylene by extended Hückel method. The results of polyethylene is the same as that by McCubbin and Manne.[25]

order approximation to the real systems.

Results and Discussion

Polysilane. The calculated band structure of polysilane is shown in Fig. 1(a). Due to the assumption of a planar-zigzag conformation, the bands form pairs degenerate at the edge of the Brillouin zone ($k=\pi/a$), where a is the lattice constant. The same kind of pairing also occurs in the results for other polymers in Figs. 1(b) and (c). The Si 3s orbitals form a broad band 1+1′. Si-H and Si-Si bonds form separated bands 2+2′ and 3+3′, respectively. These results agree with other calculations,[11–13] except that some of them indicate an overlap of the bands 2+2′ and 3+3′. We discuss this point later.

This band structure is fairly similar to that of polyethylene (Fig. 1(c)), which is the same as that by McCubbin and Manne.[25] However, the bands in polysilane show lower binding energies than corresponding ones in polyethylene. This should be due to the smaller electronegativity of Si (1.8 in Pauling scale[26]) than that of C (2.5), which appear as the smaller H_{ii} of Si 3p than that of C 2p in Table 1. Another difference is the overlap of the C-H and C-C bands (2+2′ and 3+3′) in polyethylene, which is well verified by photoemission experiments[27] and other calculations.[22]

In Fig. 2(c) we show the density of states (DOS) of polysilane derived from Fig. 1(a). The peaks in the DOS correspond to the bands in Fig. 1(a); their characters are also shown. For a comparison, in Figs. 2(a) and (b) we show the reported gas-phase UPS spectra of SiH_4[28,29] and Si_5H_{12}.[8] The peak energies in these spectra are listed in Table 2. In this comparison, the calculated DOS is rigidly shifted by 2.0 eV as described in Calculation. The studies of Si_nH_{2n+2} from $n=1$ to 5 by Bock et al.[8] revealed that the spectra of these compounds consist of (i) a largely unchanged intense peak due to the SiH bonds and (ii) split levels below and above the SiH peak, which are derived from interacting Si3s orbitals and SiSi bonds, respectively. These characters are shown in the figure.

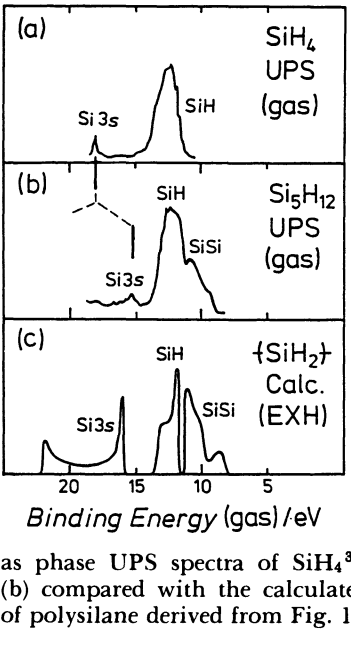

Fig. 2. Gas phase UPS spectra of SiH_4[35] (a) and Si_5H_{12}[8] (b) compared with the calculated density of states of polysilane derived from Fig. 1(a).

Since previous studies have shown that electronic structures of oligomers of 5 units already resemble that of a polymer,[30–32] a comparison between the theory and the spectrum of Si_5H_{12}, the longest silane oligomer so far measured, is meaningful for the discussion of polysilane. In Fig. 2 a good correspondence can be seen between these two, as well as an agreement of the peak assignments.

We also see a good correspondence between the band calculation and the n-dependence reported by Bock et al.[8] The large shift of the uppermost Si3s level from $n=1$ to 5 (2.86 eV) corresponds to the wide dispersion of the Si 3s band in Fig. 1(a), which reflects the strong interaction between the directly bonded Si atoms. Further, the insensitivity of the SiH peak to the chain length corresponds to the narrow width of the calculated SiH bands in Fig. 1(a), which indicates a weak interaction among the SiH bonds. These results support the absence of an overlap between the SiSi and

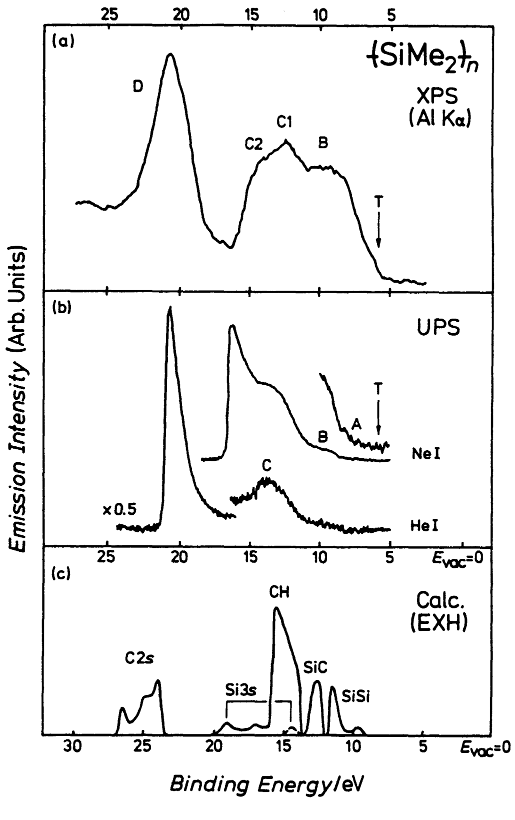

Fig. 3. X-Ray (a) and ultraviolet (b) photoelectron spectra of poly(dimethylsilane) solid compared with (c) the density of states deduced from the extended Hückel calculation in Fig. 1(b) by making a histogram of 0.5 eV steps. The abscissa is 2.5 eV shifted as described in the text. The ionization threshold and peaks are labelled T and A—D, respectively.

SiH bands in the present calculation. This absence also agrees with a recent calculation using realistic semiempirical parameters.[13] In contrast to this, the UPS spectra of short alkanes[33] show no stationary peak, because of the mixing among the electronic states derived from the CH and CC bonds.

Thus we can conclude that the important aspects of the electronic structure of polysilane are reproduced in the calculated band structure in Fig. 1(a).

Poly(dimethylsilane). In Figs. 3(a) and (b), we show the XPS and UPS spectra of PDMS. The abscissa is the binding energy relative to the vacuum level. The absolute energy scale could be accurately determined for the UPS spectra by taking the left-hand cutoff of each spectrum to be zero kinetic energy of photoelectrons.[17] The absence of charging is verified; by the sharpness of this cutoff. The energy scale of the XPS spectrum is adjusted to fit the spectral features with those in the UPS spectra.

In the XPS spectra we can see four features labelled B, C1, C2, and D. In the UPS spectra, three valence band features (A, B, and C) can be seen. Feature C corresponds to the broad band formed by C1 and C2 in the XPS spectrum. The sharp intense peak near the left-hand cutoff in the UPS spectra are due to secondary electrons. The topmost part of the valence band is not clearly seen in the UPS spectra in Fig. 3, possibly due to an incomplete cleanliness of the sample surface. Fortunately, this part (feature A) can be more clearly seen in the UPS spectra at lower photon energies (Fig. 4) with a clear onset T at 5.9±0.1 eV corresponding to the ionization threshold. The binding energies of these spectral features are listed in Table 2.

We now analyze these spectra with the aid of the calculated band structure of PDMS and the theoretical and experimental results of the relevant compounds.

The calculated band structure of PDMS is shown in Fig. 1(b). The highest occupied bands 9+9′ originate from interacting Si–Si bonds, as in polysilane. The

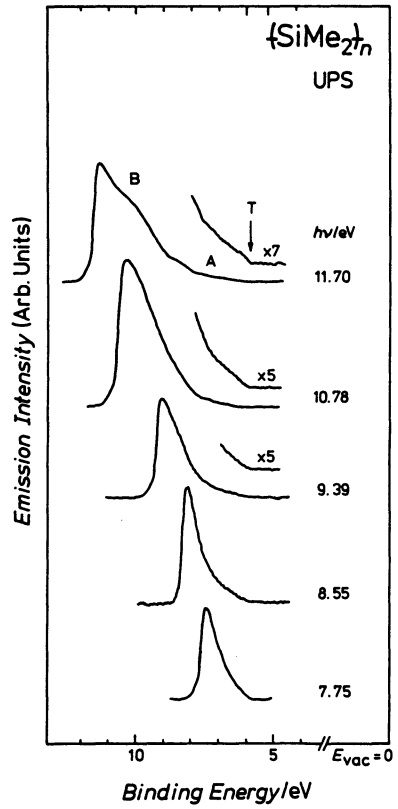

Fig. 4. Ultraviolet photoelectron spectra of poly(dimethylsilane) solid at low photon energies.

Table 2. Observed Binding Energies of the Spectral Features in the Photoelectron Spectra (in eV)

Feature	PDMS				$SiMe_4$		Si_2Me_6	Si_4Me_{10}	SiH_4	Si_5H_{12}
	XPS (solid)	label	UPS (solid)	label	XPS (gas)	UPS (gas)	UPS (gas)	UPS (gas)	UPS (gas)	UPS (gas)
Threshold	—	T	5.9	T	—	9.42[a] 9.79[a]				
SiSi			6—9	A	—	—	8.69	7.98 8.76	—	9.36 [10.1] [10.6] [10.9]
SiC	9.5	B	9.5	B	10.4	10.57	10.4	10.5	—	—
SiH	—	—	—	—	—	—	—	—	12.82	[11.8] [12.2] [12.5]
CH	12.6	C1			11.5					
			13.6	C	13.2	13.06	13.5	Not shown	—	—
	14.1	C2			14.1	14.08				
Si3*s*	12.6	C1	Not obsd.		15.5	15.58	Not obsd.	Not shown	18.16	15.3
C2*s*	20.7 22.8	D			21.72 24.0				—	—
Ref.	This work		This work		34	35	10	10	28,29	8

Values in the brackets are estimated from the deconvolution of the observed spectrum.
a) Values reported in two works in Ref. 35 obtained by different ways of extrapolation. Energies of other spectral features are almost the same.

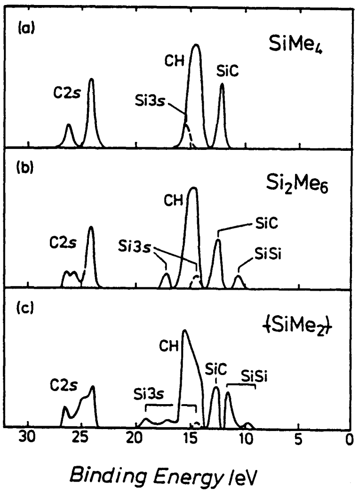

Fig. 5. Calculated density of states of $Si(CH_3)_4$ (a), $Si_2(CH_3)_6$ (b), and poly(dimethylsilane) (c).

dispersion is also farily similar to that of polysilane. The next bands 8+8′ are derived from the Si-C bonds. The next four pairs of narrow bands 4+4′—7+7′ at 15 eV originate mainly from the C-H bonds. The linear combination of Si3s orbitals form the wide band 3+3′ at ca. 17 eV. The character analysis of the bands revealed that the top of the Si band is not in 3′ at k=0 but in 6′ at k=0. This splitting originates from the avoided crossing with the CH bands with the same symmetry. Finally, the two pairs of bands 2+2′ and 1+1′ around 25 eV are derived from the C2s orbitals.

The DOS of PDMS obtained from this band calculation is shown in Fig. 3 (c) with the characters of the contributing bands. Further, in Fig. 5 we compare this DOS with those of $Si(CH_3)_4$ and $Si_2(CH_3)_6$. For the latter two, the functions located at MO binding energies are convoluted with a Gaussian function of 0.7 eV FWHM for simulating the photoelectron spectra.

As a counterpart from experimental observations, in Fig. 6 we compare our XPS and UPS spectra with the reported photoelectron spectra of permethylated silanes[10,34,35] and a long alkane n-$C_{36}H_{74}$,[36] a good model compound of polyethylene. The binding energies of the features in these spectra are listed in Table 2. The characters of each band in the reported spectra are taken from the original papers.

It is known that the photoelectron spectrum of a molecular solid fits well with the gas phase spectrum of a constituent molecule, when due allowance is made for a shift in the binding energy scale and for peak broadening.[37] Thus we can compare the observed XPS and UPS results of solid state with the gas-phase spectra and theoretical calculations (for an isolated chain) by rigidly shifting the energy scale. Since the shift comes from the polarization of the molecules surrounding the cation, it is called the polarization energy.[38] In Fig. 6, the solid spectra are shifted by 1.0 eV, which is a common value observed for other compounds.[39] In Fig. 5, the calculated DOS is shifted by 2.5 eV for the best overall fit with the XPS and UPS results. This shift contains contributions from the polarization energy and from the shift described in Calculation.

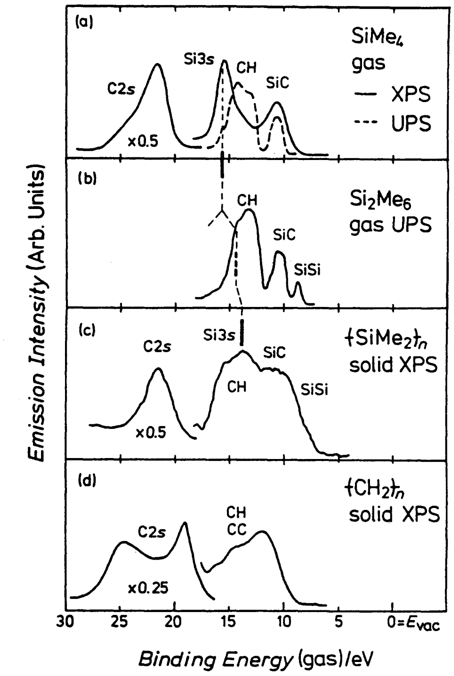

Fig. 6. Photoelectron spectra of permethylated silanes[10,34,35] and n-$C_{36}H_{74}$.[36] Solid state spectra are shifted by 1.0 eV for compensating the polarization energy. The location of the upper edge of the Si3s band is indicated.

From Figs. 5 and 6, the intense feature D in the XPS spectrum can be easily assigned to the calculated C2s bands 2+2′ and 1+1′, the latter probably corresponding to the tail at the higher-binding-energy side. The observed width (FWHM 3.3 eV) is much smaller than that of polyethylene (7.6 eV at half height) (Fig. 6(d)). Correspondingly, the calculated total width of the 1+1′ and 2+2′ bands are much smaller than that of the 1+1′ band of polyethylene. This difference can be explained by the fact that the interaction among the C2s orbitals is small in PDMS where the carbon atoms are not directly bonded, while the interaction is strong in the directly-bonded carbon chain of polyethylene.

In discussing the lower binding energy region, we at first note that the photoionization cross section of the Si3s orbital is almost negligible in the UPS region, as can be seen from a comparison of the XPS and UPS spectra of $Si(CH_3)_4$ in Fig. 6(a). Thus, we can analyze the UPS spectra in terms of the bands derived from the CH-, SiC-, and SiSi-bonds.

The calculation shown in Fig. 1(b) indicates that these bands do not overlap. In particular, each CH- and SiC-derived band shows a small dispersion. Reflecting this situation, the energies of the DOS peaks of CH and SiC character in Fig. 5 are almost independent of the silicon number, *m*.

The trends in the UPS spectra of $Si(CH_3)_4$ and $Si_2(CH_3)_6$ in Fig. 6 verify this theoretical expectation. The CH-, SiC-, and SiSi-peaks are well separated, and the energies of the former two are almost the same. We can thus assign peaks C, B, and A in the UPS spectra of PDMS to the CH-, SiC-, and SiSi-bands, respectively.

Next we discuss the levels derived from the Si 3s orbitals. The band calculation of PDMS in Fig. 1(b) shows a large dispersion of the Si3s-derived bands 3+3′, which corresponds to the strong 3s-3s interaction by the Si-Si bonds. This situation can also be seen as an increasing splitting of the DOS peaks in Fig. 5 with increasing *m* (note that the upper edge of the Si3s band is at 6′ at $k=0$). Thus, we expect a significant overlap of the CH- and Si3s-derived bands.

By comparing the UPS and XPS spectra in Figs. 2(a) and (b), we find that the upper-binding-energy part of peak C in the UPS spectrum becomes enhanced as C1 in the XPS spectrum. Thus. we can assign this enhanced peak to the upper edge of the Si3s band, and the broad background peak C1+C2 to the CH bands. The shift of the Si3s level from that of $Si(CH_3)_4$ (ca. 2 eV) due to the band formation is a little smaller than the corresponding value for polysilane (ca. 3 eV), in accordance with the calculation. The lower edge of the Si3s band is difficult to distinguish, even in the XPS spectrum. It may be buried in the tail of the intense C2s band on the low-energy side.

Finally, we discuss the inductive effect of the methyl groups. It shifts the Si-Si and Si3s levels of PDMS to a lower binding energy than those of polysilane. This shift is evaluated to be 1.6 eV from a comparison of the observed spectra of oligomers, while calculations in Fig. 1 gives a value of about 1 eV. A similar shift is also found in a recent calculation on alkyl-substituted polysilanes.[13]

Ionization Thresholds and Electrical Conductivity. Two important parameters of the uppermost band in discussing the electrical conductivity of polymers are (i) the energy of the upper edge (ionization threshold energy) and (ii) the bandwidth. The former is related to the feasibility of carrier (hole) generation by acceptor doping, while the latter is a measure of the degree of delocalization in a single chain.

In Table 3, we compare the solid ionization thresholds I_s^{th} and the widths of the highest occupied bands of PDMS, polysilane, and polyethylene.[40] Relevant data of poly(*p*-phenylene)[32] and polyacetylene[41] are also included as representatives of conduct-

Table 3. Ionization Threshold Energies and Bandwidths of Polysilane, PDMS, and Related Polymers (in eV)

Polymer	I_s^{th}/eV	Width of the highest occupied band
PDMS	5.9	2.0[e]
Polysilane	(7.5)[a]	2.0[e]
Polyethylene	8.5[b]	4.0[f]
Polyacetylene	5.24[c]	5—6[c]
Poly(*p*-phenylen)	5.6_5[d]	3.9[d]

a) Estimated from the value of PDMS assuming a shift of 1.6 eV. b) Ref. 40. c) Ref. 41. d) Ref. 32. e) Estimated from the UPS spectra of oligomers. f) Ref. 27.

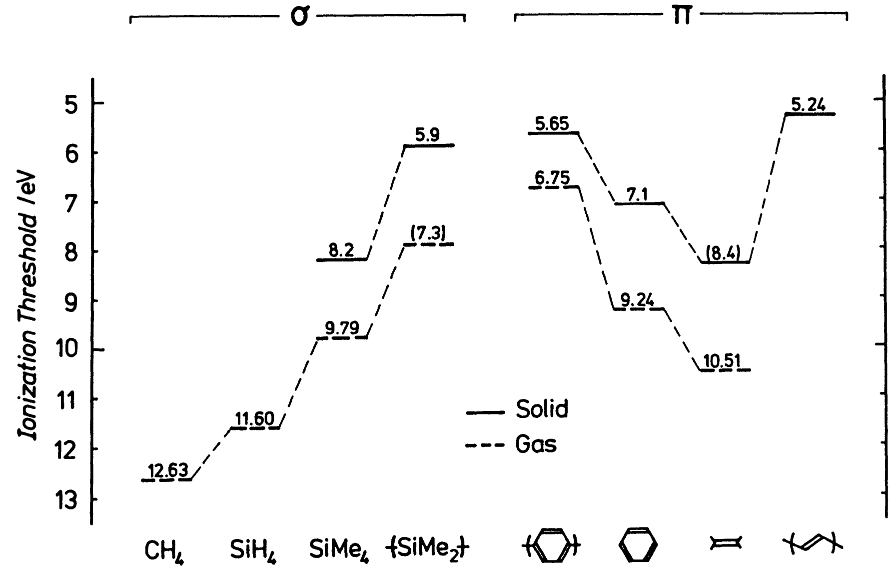

Fig. 7. Ionization thresholds of σ-conjugated silanes and π-conjugated hydrocarbons. For comparison, the data of CH_4 is included in the σ-system. The data in the parentheses are estimated by assuming a gas-to-solid difference in the adjacent compound in the figure. Values not listed in Tables 2 and 3 are taken from the following: CH_4: Ref. 43 (gas); $Si(CH_3)_4$: Ref. 44 (solid); poly(*p*-phenylene): Ref. 32 (gas); benzene: Refs. 43 (gas) and 45 (solid); ethylene: Refs. 43 (gas) and 46 (solid).

ing polymers with a π-conjugated carbon principal chain. The ionization threshold of polysilane is estimated from the value of PDMS, assuming a 1.6-eV shift due to the inductive effect by the methyl groups. Although a precise determination of the band widths is difficult for PDMS and polysilane, we can still estimate them to be of the order of ca. 2 eV from the spectra of PDMS (Fig. 4) and oligomers. The value of polyacetylene was also deduced from the data of oligomers.[42)]

In Table 3 we can see that the threshold of polysilane is 1 eV smaller than that of polyethylene due to the smaller electronegativity of Si than C (as discussed above). Further, the value of PDMS is 1.6 eV smaller than that of polysilane by the inductive effect of methyl groups, and almost comparable to that of poly(*p*-phenylene). However, it is still significantly larger than that of polyacetylene, which can be doped with iodine. This is consistent with the experimental results that doping of PDMS needs strong acceptors, such as AsF_5 and SbF_5.[1)]

In Fig. 7 the change of ionization thresholds of σ-conjugated systems from CH_4 to PDMS are compared with analogous change in π-conjugated hydrocarbon systems. In the latter, the orbital energies of the highest occupied orbital is lowered by a strong (4 to 5 eV bandwidth) π conjugation. Note that the ionization threshold of the solid polymers are smaller than the value of gas phase due to the polarization energy.

The bandwidths of polysilane and PDMS are less than those of π-conjugated polymers. However, such bandwidths should still be sufficient for realizing a good intrachain conductivity, since they are already much larger than the bandwidths of conducting molecular complexes.[47)] Therefore, the origin of the limited conductivity of doped PDMS (7×10^{-3} S cm^{-1})[1)] may be a small interchain conductivity. Although permethylation is advantageous for a high intrachain conductivity by lowering the ionization threshold, the methyl groups hinder the hole transport from chain to chain. The increased conductivity of photo-crosslinked polymers[1)] supports this idea. Another possible way of increasing the interchain conductivity will be the partial substitution of PDMS by some pendant group which can "shake hands" to transport the holes. However, the conductivities of doped phenyl-substituted PDMS are lower than that of doped PDMS.[1)] Therefore, the choice of an appropriate pendant for such a purpose needs further consideration.

Concluding Remarks

In this paper we reported a combined theoretical and experimental study of polysilane and poly(dimethylsilane) (PDMS). Observed XPS and UPS spectra of PDMS could be analyzed in a detailed way by theoretical band calculations. Further, a comparison with oligomers confirmed the assignments and also revealed how the electronic structures of these polymers evolve from those of constituent units. Such a successful use of oligomers for studying the Si-backboned polymers is an extension of similar studies for polymers with carbon-derived backbones, where the usefulness of oligomers has been already well demonstrated.[27,30–32)]

Polysilane and PDMS have rather small ionization energies due to the small electronegativity of Si, σ-delocalization and the inductive effect of methyl groups. Although the one-dimensional delocalization makes the ionization energy still larger than that of a three-dimensionally connected Si solid (5.35 eV),[48)] the value of PDMS is already comparable to those of π-conjugated carbon-derived polymers. This fact explains the good conductivity to PDMS and its derivatives upon doping. Further, the linear structure offers useful properties such as the solubility to organic solvents.

Thus, the introduction of Si as a constituent atom of the principal chain offers an exciting prospect for designing materials of interesting electronic properties. Although in this work we have dealt with the most basic two polymers of this group, other interesting derivatives, e.g. with π-pendants, have also been synthesized.[1)] A study of the electronic structures of such polymers will give more insight into the full possibilities of polysilanes. The work of Loubriel and Zeigler[14)] pioneered this direction, and recently we have also examined the chain-pendant interaction in poly(methylphenylsilane) in some detail.[49)]

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