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Valence electronic structures of organopolysilanes having symmetric alkyl side-chains studied by x-ray photoelectron spectroscopy

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Abstract. The valence electronic structures of organopolysilanes having symmetrical alkyl side-chains, i.e., poly(di-*n*-alkyl silanes) $[\text{Si}(\text{C}_n\text{H}_{2n+1})_2]_m$, have been systematically studied by x-ray photoelectron spectroscopy (XPS) for the first time. The specimens used in this work are poly(di-methyl silane) $[\text{Si}(\text{CH}_3)_2]_m$, poly(di-ethyl silane) $[\text{Si}(\text{C}_2\text{H}_5)_2]_m$, poly(di-pentyl silane) $[\text{Si}(\text{C}_5\text{H}_{11})_2]_m$, poly(di-hexyl silane) $[\text{Si}(\text{C}_6\text{H}_{13})_2]_m$ and poly(di-decyl silane) $[\text{Si}(\text{C}_{10}\text{H}_{21})_2]_m$. By comparing the XPS spectra of the poly(di-*n*-alkyl silanes) with those of normal alkanes, it is found that the spectral features are strongly affected by two factors, i.e., the carbon 2s and 2p electrons in the side-chains and the silicon 3s and 3p electrons in the backbone. The shape of the spectrum from 0 to 5 eV, which is strongly affected by the structure of the valence band edge, shows no significant change with a change in the number of carbon atoms in the alkyl substituents. On the other hand, the splitting of the carbon 2s orbitals in the side-chains strongly affects the shape of the spectrum in the region from 12 to 20 eV. The results are also discussed on the basis of the theoretical calculations as well as the ultraviolet photoelectron spectrum reported previously.

1. Introduction

Organopolysilanes are chainlike polymers which consist of a silicon backbone and side-chains of organic substituents (see figure 1). In the backbone, the bonded σ electrons are well delocalized along the chain direction, so the structure is considered to be a quasi-one-dimensional electronic system. In this case, the word ‘delocalization’ means the spread of the wavefunction, and the degree of the delocalization depends on the structural order and the conformation of the silicon backbone [1]. Up to the present time, many interesting physical properties have been reported for the organopolysilanes [2, 3]. For example, they are considered to be direct-allowed-gap semiconductors, and show an efficient photoluminescence [4]. Therefore, the organopolysilanes are expected to be used for various optical and electronic devices as novel materials [1].

In order to find the way from the new materials to applicable devices, it is quite important to investigate their electronic states, particularly the structure and the properties of the

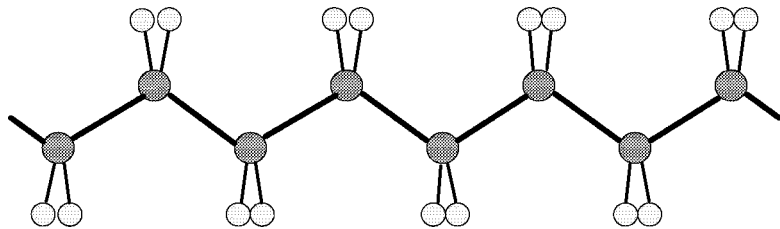


Figure 1. Structure of poly(di-methyl silane). Large and small circles indicate Si and CH₃, respectively.

occupied states. From this point of view, various theoretical band calculations have been performed by many researchers [5–8]. These results indicated that the electronic structure of organopolysilanes is similar to that of direct-allowed-gap semiconductors, whereas single-crystal silicon has an indirect gap. The conditions which lead to the interaction between the delocalized σ electrons in the silicon backbone and the electrons in the side-chains have also been reported [9].

On the other hand, various photoelectron spectra have been reported in order to investigate the valence electronic structures of organopolysilanes experimentally [7–11]. From these experimental data, it was suggested that the electronic interaction between the backbone and the side-chains occurred in the organopolysilanes having aryl substituents, whereas no significant change in the shape of the photoelectron spectra was reported in the organopolysilanes without aryl substituents [9]. However, the effects of the difference of the substituents on the valence band structure have not yet been examined experimentally. Moreover, in the photoelectron spectroscopy measurements, the photoelectron intensity depends on the nature of the elements and their orbitals as well as the ionization cross-section, which varies with a change in the excitation energy.

In this paper, x-ray photoelectron spectroscopy (XPS) measurements of the valence band of poly(di-alkyl silanes) have been systematically performed for the first time. Most of the previous photoelectron spectra for the organopolysilanes were obtained by means of ultraviolet photoelectron spectroscopy (UPS). XPS has the advantage of greater contrast in ionization cross-section (see table 1), so the effect of the silicon atom on the valence band structure can be more readily determined. In order to examine the influence of the electrons of the atoms in the side-chains on the spectrum, the number of carbon atoms in the alkyl substituents was systematically changed. The spectra obtained are compared with those of normal alkanes and the theoretical band structures reported previously.

2. Experiment

As stated in the introduction, the samples prepared are poly(di-methyl silane) [Si(CH₃)₂]_m, poly(di-ethyl silane) [Si(C₂H₅)₂]_m, poly(di-pentyl silane) [Si(C₅H₁₁)₂]_m, poly(di-hexyl silane) [Si(C₆H₁₃)₂]_m and poly(di-decyl silane) [Si(C₁₀H₂₁)₂]_m. These were synthesized by Wurtz-type reductive coupling of corresponding dichlorosilanes. In order to remove the remaining impurities, poly(di-pentyl silane), poly(di-hexyl silane) and poly(di-decyl silane) powder were dissolved in toluene, and washed with purified water before the XPS measurements. No extra purification was carried out for poly(di-methyl silane) or poly(di-ethyl silane) after the synthesis.

The XPS spectra were measured with a Shimadzu ESCA-850 photoelectron spectrometer

Table 1. Ionization cross-sections of the Si 3p, Si 3s, C 2p and C 2s orbitals for the typical energy values of the excitation source for both the XPS and UPS measurements. The values are normalized relative to those of Si 3p (see [12]).

Orbital	Binding energy (eV)	Ionization cross-section σ		
		$h\nu = 21.2$ eV (UPS)	$h\nu = 40.8$ eV (UPS)	$h\nu = 1253$ eV (XPS)
Si 3p	3	1.00	1.00	1.00
Si 3s	8	0.976	1.04	4.64
C 2p	6	13.4	4.52	0.120
C 2s	17.5	3.73	3.56	3.10

using Mg $K\alpha$ x-ray radiation (photon energy: 1253.6 eV) as an excitation source. The operating voltage and current of the x-ray gun were 8 kV and 30 mA, respectively, which caused no damage to the samples. The powder samples were pressed into a pellet, and fixed on the stainless steel holder by double-sided conductive tape. Wide spectral surveys in the region of binding energies from 1100 to 0 eV were performed before measuring the core levels and valence band in detail. In each spectrum, peaks attributed to core levels of Si 2s, Si 2p, and C 1s as well as the weak peak attributed to O 1s were observed. Because the ionization cross-section of the O 1s electrons is about 3.4 times as large as that of the Si 2p electrons, the content of the oxygen atoms in the samples was estimated to be a few per cent. No further remarkable photoelectron band originating from the impurities was observed. The spectrum of the Fermi edge of Au foil was also measured, and was compared with those of the poly(di-alkyl silane) specimens set on the surface of the Au foil in order to correct for the electronic charging effect, which appears in organic or insulating materials during the XPS measurements. For these measurements, the surface of the Au foil was cleaned by acetone. Then, the powder specimen was spread onto the surface of the Au foil, and was pressed by a couple of polished stainless dies. The Au foil was in contact with the sample holder, and was partly supported by double-sided conductive tape on the holder.

The ionization cross-sections of the Si 3p, Si 3s, C 2p and C 2s electrons for typical energy values of the excitation source for both the XPS and UPS are shown in table 1 [12]. According to these values, the ratios of the ionization cross-sections $\sigma(\text{Si } 3p)/\sigma(\text{C } 2p)$ and $\sigma(\text{Si } 3s)/\sigma(\text{C } 2p)$ for x-rays are much larger than those for ultraviolet light. This indicates that x-rays are suitable for the measurements of the Si 3p and Si 3s orbitals, which affect the electronic structure of the polymer.

3. Results and discussion

Figure 2 shows the XPS spectra corresponding to the valence band of poly(di-methyl silane), poly(di-ethyl silane), poly(di-pentyl silane), poly(di-hexyl silane) and poly(di-decyl silane) powder. In each spectrum, fundamental structures are separated into two parts. The spectral structures in the region of binding energies from 12 to 20 eV clearly reflect the difference in the number of carbon atoms in the substituents. The spectrum of poly(di-methyl silane), which contains one carbon atom in the substituent, shows one symmetric peak in the region from 12 to 20 eV. In the spectrum of poly(di-ethyl silane), two peaks are observed in this region. A broad band having a width of about 9 eV is observed for poly(di-pentyl silane), poly(di-hexyl silane) and poly(di-decyl silane) in the region from 12 to 20 eV.

Figure 3 shows the XPS spectra of normal alkanes which were reported by Pireaux *et al*

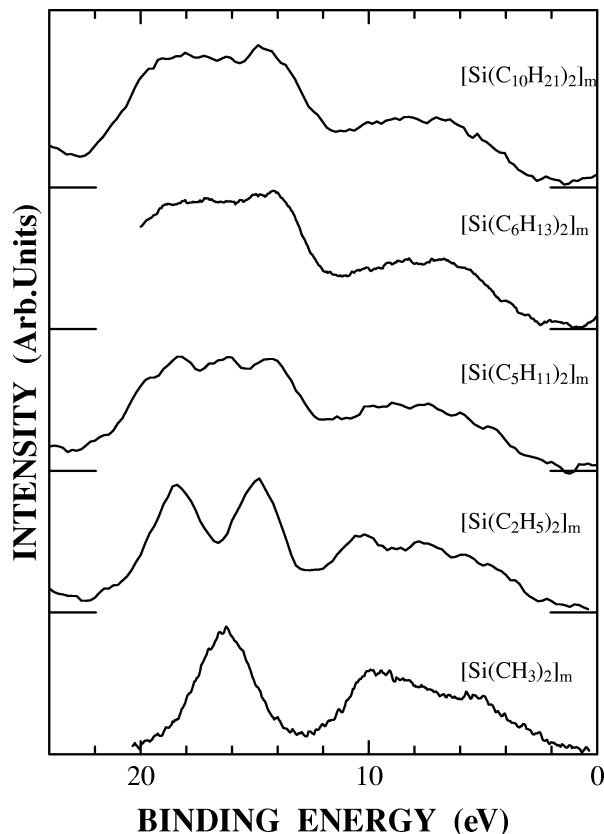


Figure 2. X-ray photoelectron spectra of poly(di-alkyl silane) powders. The band in the region from 12 to 20 eV mainly originates from the C 2s orbitals of the side-chains. The spectra in the region under 5 eV do not differ much.

[13, 14]. In figure 3, the spectra of methane, CH_4 , and ethane, C_2H_6 , were measured in the gas phase, whereas the others were measured in the solid phase. The XPS data of the normal alkanes in the gas phase show only trivial shifts of the binding energies (see the lower scale in figure 3) compared with those measured in the solid phase (see the upper scale in figure 3) due to the decrease of the polarization effect in the gas phase [14]. The spectral structures of the alkanes were assigned to two bands, i.e., C 2s and C 2p [13, 14]. In the region from 12 to 20 eV (solid phase) or from 18 to 28 eV (gas phase), the shapes of the spectra are similar to those of the corresponding poly(di-alkyl silanes) shown in figure 2. Therefore, it is concluded that the peaks for the poly(di-alkyl silanes) appearing from 12 to 20 eV in figure 2 originate from the C 2s orbital of the side-chains. The splitting of the peaks in the spectra in figures 2 and 3 is caused by the splitting of the C 2s orbital with an increase in the number of carbon atoms in the side-chains.

In the region of binding energies from 5 to 11 eV, changes of the spectral shapes of the poly(di-alkyl silanes) are also observed depending on the number of carbon atoms in the side-chains. For poly(di-methyl silane), the peaks appearing in this region were assigned by Seki *et al* [8]. Using their assignments, peak separation was performed for poly(di-methyl silane) and poly(di-ethyl silane), and the results are shown in figure 4. The solid curves indicate experimentally obtained spectra, which are the same as those shown in figure 2.

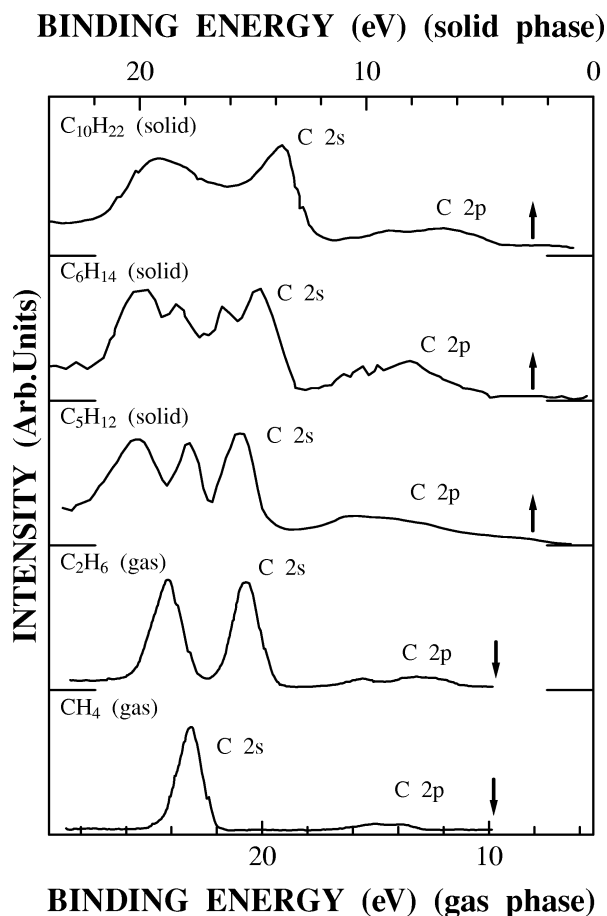


Figure 3. X-ray photoelectron spectra of the normal alkanes reported by Pireaux *et al* [13, 14]. The spectra of CH_4 and C_2H_6 were measured in the gas phase, whereas the others were measured in the solid phase. The scales for gas and solid phases are shown on the lower and upper horizontal axes, respectively.

The dashed and dotted curves in figure 4 indicate the contribution of each orbital, obtained by assuming Gaussian peaks for the Si 3p, Si 3s and C 2p orbitals. The dashed curves indicate the Si 3p, Si 3s peaks, and dotted curves show the C 2p peaks. As shown in figure 4, the shape of the spectrum of the poly(di-ethyl silane) is different from that of the poly(di-methyl silane) in the region from 6 to 10 eV. This spectral feature is well understood by considering the magnitude of the C 2p peak at 7.8 eV. This is because the number of carbon atoms in the poly(di-ethyl silane) is twice as large as in the poly(di-methyl silane).

The results of the peak separation were also compared with those of the recent theoretical energy band structure calculated by means of the valence effective Hamiltonian (VEH) technique [15]. The previous theoretical and the present experimental results are summarized in table 2. The band width of the separated peaks described by the full width at half maximum (FWHM) is in good agreement with the value of the previous theoretical result obtained using the VEH technique.

Figure 5 shows the XPS spectra of poly(di-hexyl silane) and the corresponding normal

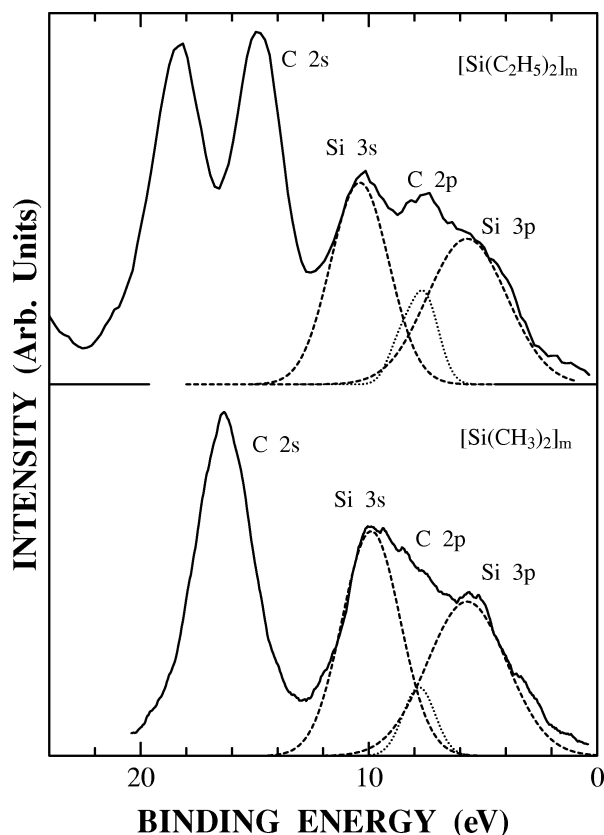


Figure 4. Results of the peak separation for the spectra of poly(di-methyl silane) and poly(di-ethyl silane). The solid curves indicate experimentally obtained spectra, which are the same as those shown in figure 2. The dashed and dotted curves indicate the contribution of each orbital, obtained by assuming Gaussian peaks for the Si 3p, Si 3s and C 2p orbitals.

Table 2. Results of the peak separation for poly(di-methyl silane) and poly(di-ethyl silane). VEh means the valence effective Hamiltonian technique (see [15]).

Specimen	Orbital	FWHM (eV) (XPS)	Peak width (eV) (VEH)
[Si(CH ₃) ₂] _m	Si 3p	4.1	4.71
	Si 3s	3.0	3.66
	C 2p	1.6	1.31
[Si(C ₂ H ₅) ₂] _m	Si 3p	4.1	4.40
	Si 3s	3.0	3.56
	C 2p	1.9	3.35

alkane, C₆H₁₄. The previously reported UPS spectrum for poly(di-hexyl silane) using 40 eV light as an excitation source is also shown in figure 5 [10]. For the upper spectrum, peak separation was performed for the Si 3s and Si 3p orbitals, and the results are shown by the dashed curves. The dotted curve in the upper figure shows the residual component of the spectrum, so the dotted curve is considered to be due to the C 2p orbital. The

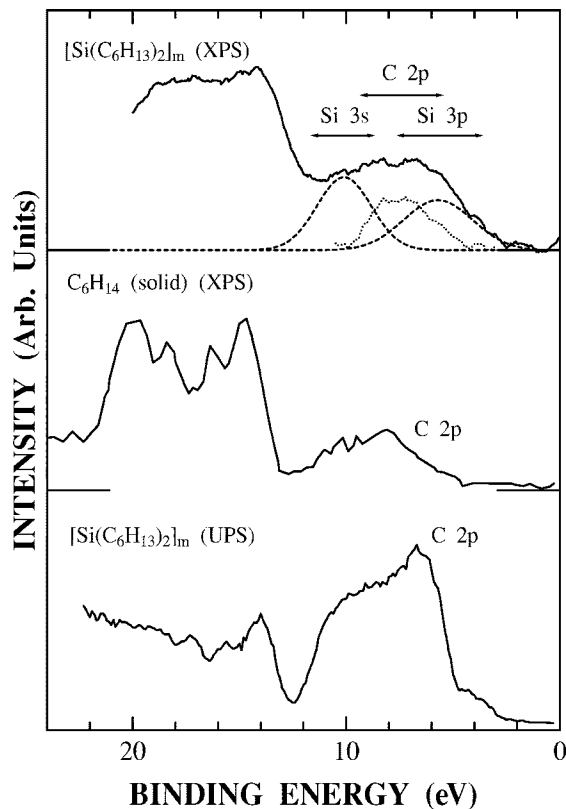


Figure 5. XPS spectra of poly(di-hexyl silane) and the corresponding normal alkane, C_6H_{14} . The dashed curves in the upper figure show the results of the peak separation performed for the Si 3s and Si 3p orbitals. The dotted curve in the upper figure shows the residual component of the spectrum, so the dotted curve is considered to be due to the C 2p orbital. The lower figure shows the UPS spectrum reported by Seki *et al* [10].

shape and the energy value of this residual component are almost the same as those of the spectrum obtained for the corresponding normal alkane, C_6H_{14} . This indicates that the analysis performed in figure 4 is reasonable. The results are also compared with the UPS spectrum [10]. In the UPS spectrum, a strong peak is observed at 6.5 eV. By comparing the spectrum with the XPS data, this peak is attributed to be C 2p orbitals, because the ionization cross-section for the C 2p orbitals is much greater than those of the Si 3p and Si 3s orbitals for ultraviolet light.

Figure 6 shows the band widths of the peaks described by the FWHM for the Si 3p, 3s and C 2p orbitals obtained from the peak separation. These are plotted as a function of the number of carbon atoms in the side-chains. The open circles and open triangles show the values for the Si 3p and Si 3s orbitals, respectively. The closed circles indicate the band width for the C 2p orbitals. The values of the band widths for the Si 3p and Si 3s orbitals are not much changed, whereas those for the C 2p orbital increase with an increase in the number of carbon atoms. This increase of the width of the C 2p band is in good agreement with the previously reported band broadening of the C 2p orbitals for the normal alkanes [13]. Therefore, it is concluded that the change of the valence electronic structure of the poly(di-alkyl silanes) is mostly caused by the change of the number of carbon atoms in the

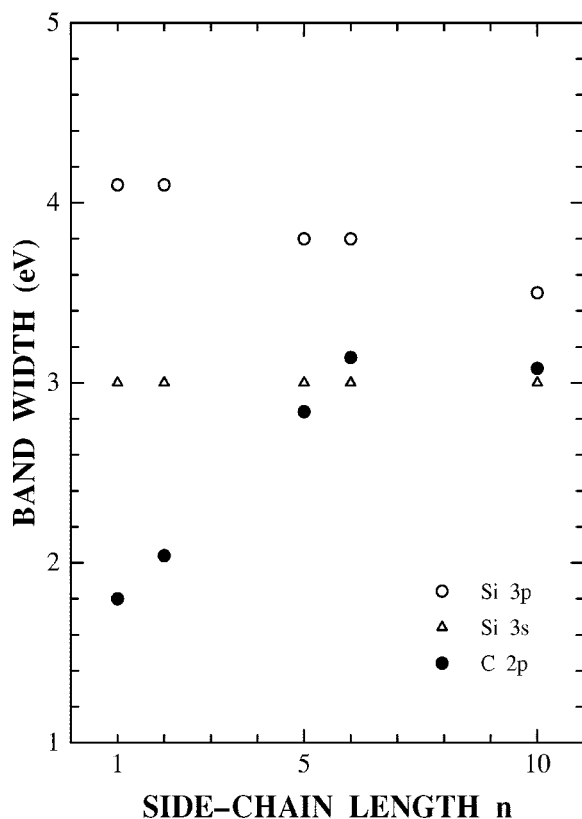


Figure 6. Band widths of the peaks for the Si 3s, Si 3p and C 2p orbitals described by the FWHM as a function of the number of carbon atoms in the side-chains. These were obtained by peak separation.

side-chains. In this case, the Si 3p and 3s orbitals are hardly affected by the difference of the side-chains. Similarly, no significant spectral change is observed in the region under 5 eV, which corresponds to the top of the valence band.

4. Summary and conclusion

The XPS spectra corresponding to the valence band of the poly(di-alkyl silanes) have been systematically measured for the first time. The effect of the difference of the alkyl substituents was clearly observed in the region of binding energies from 12 to 20 eV. Splitting of the spectrum was observed in this energy region, due to the C 2s electrons. The change of the spectral shape from 6 to 10 eV was also observed, attributed to the changes of the relative intensity and the band width of the component originating from the C 2p electrons with an increase in the number of carbon atoms in the side-chains. On the other hand, no significant spectral change was observed in the region under 5 eV, which corresponded to the top of the valence band, and was mostly determined by the Si 3p electrons.

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