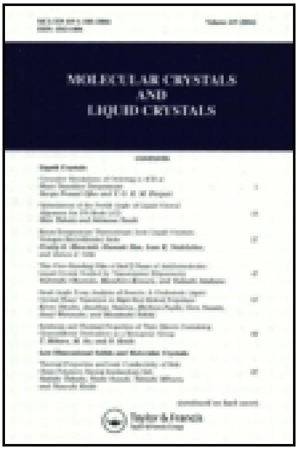

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ELECTRONIC STRUCTURES OF SILICON-BASED ORGANIC COMPOUNDS STUDIED BY UV PHOTOEMISSION

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ABSTRACT The electronic structures of five polysilanes and octa(*t*-butyl)octasilacubane were investigated by ultraviolet photoemission spectroscopy (UPS). The spectral features were assigned by comparison with spectra of the constituents parts. The UPS spectra of the polyalkylsilanes indicate that the valence electronic structure can be regarded as an overlap of those of the Si-backbone and substituents. In the case of polyarylsilanes, all the spectral features except those in the uppermost energy region correspond one by one to each band in the spectra of the substituents as in the case of polalkylsilanes. The deviation of the spectral features in the uppermost energy region from those of the constituents suggests σ–π interaction between the πHOMO states of benzene and the Si σHOVB states of the Si backbone. The results of octa(*t*-butyl) octa-silacubane are also discussed.

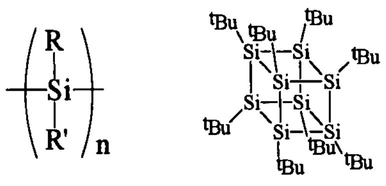
INTRODUCTION

Silicon-based organic materials, whose electronic structure is characterized by σ-conjugation along the Si backbone instead of π-conjugation in carbon-based materials, have attracted much attention as a class of organic-inorganic hybrid system[1,2]. Especially, polysilanes and silacubanes which have silicon backbone with lower dimension than 3- dimensional crystalline silicon, are expected to have new function in relation to quantum wire and dot. For increasing the possibility of the application of such compounds to a device material, suitable substitution of side-group is necessary to make it soluble in device-fabrication process. Thus the elucidation of the electronic structures and their change by side-group substitution is indispensable for basic understanding and application of such compounds. As far as polysilanes, several studies have been made on the valence electronic structure using ultraviolet photoemission spectroscopy (UPS)[3-5]. In a part of the spectra, however, fine structures were smeared out probably due to sample degradation by air exposure or due to charging effect.

In the present study, we investigated the whole valence electronic structure of three polyalkylsilanes, two polyarylsilanes, and octa(*t*-butyl)octasilacubane(OTBOSC), using ultraviolet photoemission spectroscopy (UPS). By careful sample preparation in nitrogen environment, we could successfully measured the UPS spectra with fine structures. The spectral features were assigned by comparison with those of the constituents parts. The effect of substitution of side-group to the electronic structure was discussed.

EXPERIMENTAL

The UPS spectra were measured by using angle-resolved UPS system at the beamline 8B2 of UVSOR at IMS[6]. All the sample were synthesized at NTT. Their chemical structures are shown in figure 1. The sample films were prepared by spin-coating of 0.4 weight % toluene solution of each compounds onto Cu substrates in a glove bag under nitrogen gas flow. These films were transferred into the vacuum chamber without exposure to air, evacuated and measured. Photoelectron was analyzed with a concentric hemispherical analyzer, with a total energy resolution of 0.2 eV.



(a) (b)

Figure 1. The chemical structure of polysilane (Fig.1a) and OTBOSC (Fig.1b).

RESULTS AND DISCUSSION

Polyalkylsilanes

The UPS spectrum (hν=40eV) of poly(methylpropylsilane) [PMPS, $(SiMePr)_n$] is shown in figure 2(a). The abscissa is the binding energy relative to the vacuum level. In order to assign the spectral features, we also show the UPS and XPS gas-phase spectra of CH_4[7,8], C_3H_8[8,9], and $Si_4(CH_3)_{10}$[10] as model compounds of the side group and the Si backbone in fig 2.(b)-(f). The spectrum has better quality than the reported one[3] and enables detailed analysis of the spectrum. As seen in the figure, the spectrum of $(SiMePr)_n$ corresponds well to the superposition of those of model compounds. This indicates that the valence electronic structure can be regarded as an overlap of those of the constituent parts.

Similar results were obtained for poly(dibutylsilane) and poly(dihexylsilane). It should be noted that the bands from alkyl group does not overlap with those of Si 3p derived states. This result indicates that the states of alkyl side group scarcely contribute to the uppermost valence electronic structure which mainly dominates the various properties of polysilanes.

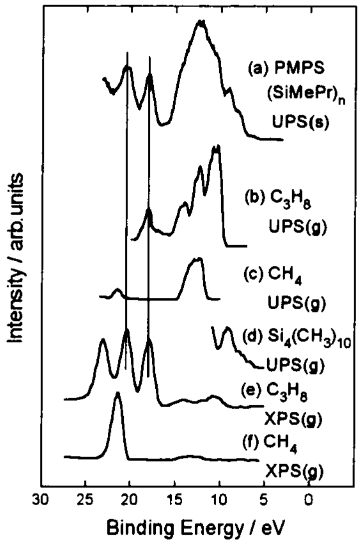


Figure 2. UPS and XPS spectra of $(SiMePr)_n$ and related compounds. (s) and (g) stand for solid and gaseous states, respectively. The gas-phase spectra are aligned to (a) at the C2s peaks as shown by vertical lines.

Polyarylsilanes

The UPS spectrum of poly(methylphenylsilane), [PMϕS, $(\mathrm{SiMe}\phi)_n$] is shown in figure 3(a) with the UPS and XPS spectra of $\mathrm{Si_4(CH_3)_{10}}$[10], $\mathrm{C_6H_6}$[11] and $\mathrm{CH_4}$[7,8] in Fig.3(b)-(e). The spectrum has better quality than the reported one again[3]. All bands of $(\mathrm{SiMe}\phi)_n$ except those in the uppermost energy region correspond one by one to each band in the spectra of the substituents. Similar result was obtained in the case of poly(di(4-ethylpheyl)silane). This indicates that the valence electronic structures of polyarylsilanes in higher binding energy region can be regarded mostly as an overlap of those of their constituents as in the case of polyalkylsilanes. The deviation of the spectral features in uppermost energy region from those of the constituents suggests σ-π interaction between the πHOMO states of benzene and the Si σHOVB states of the Si backbone. This results correspond to that of previous theoretical band calculation[4].

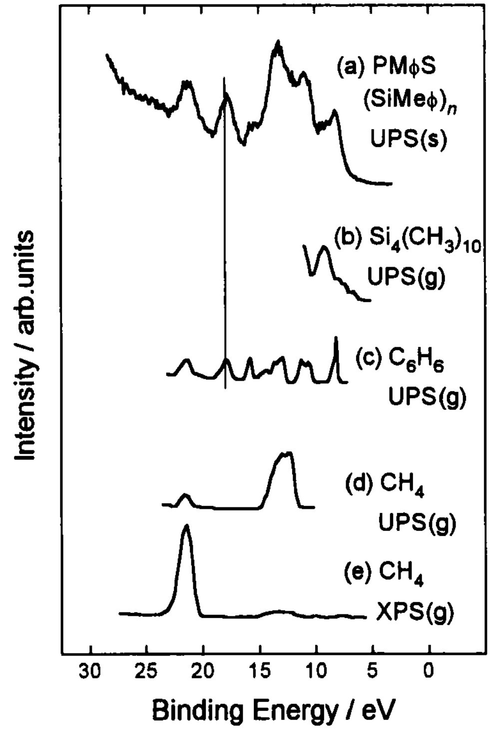


Figure 3. UPS and XPS spectra of $(\mathrm{SiMe}\phi)_n$ and related compounds. (s) and (g) stand for solid and gaseous states, respectively. The gas-phase spectra are aligned to (a) at the C2s peaks as shown by a vertical line.

Octa(*t*-butyl)octasilacubane

OTBOSC is a unique molecule consisting of silicon cube which can be regarded as a quantum dot. The UPS spectrum is shown in figure 4(a). By comparison with the UPS spectra of $Si_4(CH_3)_{10}$[10], i-C_4H_{10}[12] in Fig.4(b) and (c), the spectral features of OTBOSC could be assigned as follows; The topmost structures in the region of 5 to 9 eV are due to Si 3p derived states of cubic silicon backbone and C 2p derived states of i-C_4H_{10} due to 9 to 15 eV. The features in higher binding energy region than 15 eV are ascribed to C 2s derived states. The ionization potential determined by the onset energy of UPS was 5.2 eV. Such a smaller value than crystalline silicon (5.35 eV[13]) can be explained by effective interaction between Si atoms due to 3-dimensional configuration and inductive effect by *t*-butyl groups.

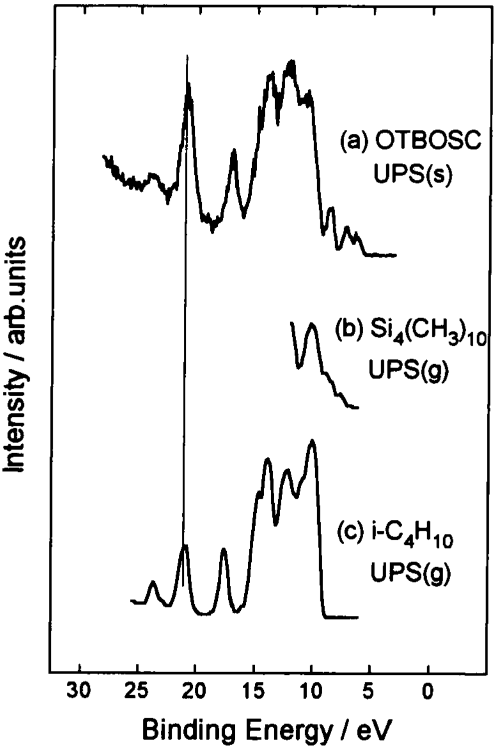


Figure 4. UPS spectra of octa(*t*-butyl)octasilacubane and related compounds. (s) and (g) stand for solid and gaseous states, respectively. The gas-phase spectra are aligned to (a) at the C2s peaks as shown by a vertical line.

CONCLUSION

UV photoemission spectra of three polyalkylsilanes, two polyarylsilanes, and ocata(*t*-butyl)octasilacubane with Si backbone were measured. Their valence electronic structure can be mostly regarded as an overlap of those of their constituents. However, the substitution of side-group induces the change of the topmost valence electronic structure, in the case of polyarylsilanes and silacubane.

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