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Abstract. Near-edge x-ray absorption fine structure (NEXAFS) has been applied to the elucidation of the geometrical structures for condensed layers of $Si(CH_3)_nCl_{4-n}$ ($0 \leqslant n \leqslant 4$). For compounds containing both methyl and chlorine groups ($n = 1, 2, 3$), it was observed that the NEXAFS at the Si K edge split into two σ^* resonances which correspond to the excitations from Si 1s to the unoccupied molecular orbitals of the Si–Cl and Si–C bonds, respectively. The polarization dependence of the intensity of the two resonances was observed only for $Si(CH_3)_3Cl$. On the basis of the incidence-angle dependences of NEXAFS peak intensities, it was concluded that the Si–Cl bond in $Si(CH_3)_3Cl$ is parallel to the surface and the average angle between surface normal and three Si–C bonds is about 43°.

1. Introduction

Synchrotron radiation is useful for elucidating geometrical structures of molecules adsorbed on a solid surface. The method referred to as near-edge x-ray absorption fine structure (NEXAFS) (sometimes this term is included in the more widely used term x-ray absorption near-edge structure (XANES)) has been extensively applied to the elucidation of the molecular orientation of adsorbates [1–3]. The principle is mainly based on the dipole selection rules governing K-shell resonance excitations; the resonance intensity associated with a specific molecular-orbital final state is the largest if the electric vector (E-vector) points in the direction of that molecular orbital into which the 1s electron is excited, and the intensity vanishes if the E-vector is perpendicular to the direction of that orbital. Therefore, most of the NEXAFS work to data has dealt with adsorbed molecules having double or triple bonds with p-derived unoccupied orbitals in different directions, i.e. σ^* and π^* orbitals [3].

When an adsorbed molecule consists of only a σ bond, on the other hand, the NEXAFS generally exhibits a single resonance peak. There have been some attempts to determine the geometrical structures of molecules without π orbitals by measuring the polarization dependences of the single-peak intensity [4, 5]. However, this method contains uncertainty derived from the normalization of the photon intensity and the possible underlying surface extended x-ray absorption fine structure [4].

In the present paper, we present examples in which we can simultaneously determine the orientations of two different molecular axes in a molecule which has only σ bonds. The principle of the method is basically the same as that of ordinary NEXAFS, but the important point is as follows. If a central atom in a molecule is coordinated to two kinds of atom or group in different directions and we can separate the energy of the resonance excitation from the core to unoccupied molecular orbitals composed of the respective two groups, it is

possible to determine the molecular orientation by comparing the polarization dependences of the two resonance intensities.

As an example, methychlorosilane molecules, $Si(CH_3)_3Cl$, $Si(CH_3)Cl_3$ (C_{3v} symmetry), and $Si(CH_3)_2Cl_2$ (C_{2v} symmetry), are chosen in the present study. In these molecules, a central silicon atom is coordinated to methyl and chlorine groups with different symmetries. For comparison, the NEXAFS of non-mixed compounds such as $Si(CH_3)_4$ and $SiCl_4$ (T_d symmetry) are also investigated. As a result, we have observed a strong polarization dependence of the NEXAFS at the Si K edge for the condensed layer of $Si(CH_3)_3Cl$ molecules. The angles between the surface and the Si–Cl or Si–C bond are simultaneously determined on the basis of the polarization dependences of the resonance peak intensities in the NEXAFS spectra.

2. Experimental details

The experiments were performed at the BL-27A station of the Photon Factory in the National Laboratory for High-Energy Physics. Two single crystals of InSb(111) were used as a monochromator whose energy resolution was about 0.9 eV at 2 keV and 1.4 eV at 3 keV photon energy.

A Cu(110) substrate was cleaned by repeating the sputtering with 500 eV Ar^+ ions and annealing at 600 K in oxygen at 10^{-4} Pa. Its periodicity and cleanliness were checked by low-energy electron diffraction and x-ray photoelectron spectroscopy (XPS), respectively. In order to check the effect of the substrate on the molecular orientation of the multilayer, Ni(111) and Pt(111) were also used as substrates.

The high-purity solution of $Si(CH_3)_nCl_{4-n}$ ($0 \leqslant n \leqslant 4$) molecules was degassed and used to dose the substrate at 90 K through a microchannel-plate gas doser located 10 mm in front of the surface. To obtain a layer of reproducible thickness, the pressure in the gas inlet system was kept at 1.0 Pa, while the valve to the gas doser was opened for distinct periods of time. The thickness of the adsorbed layer was precisely determined by *temperature-programmed desorption* (TRD) *measurements.*

The NEXAFS was measured by recording the intensity of secondary electrons at a fixed energy (partial electron yield mode) as a function of the photon energy. Since the kinetic energy of Auger electrons sometimes shifts around the resonance photon energy [6, 7], the kinetic energies of the secondary electrons were adjusted to be slightly lower than those of the respective KLL Auger electrons, i.e. 1500 eV for Si K-edge NEXAFS and 2040 eV for Cl K edge NEXAFS. The partial electron yield was normalized by the photon intensity which was monitored with a copper mesh located in front of the sample. The photon energy was calibrated with a hemispherical electron energy analyser using Au $4f_{7/2}$ photoelectrons ($E_b = 84.0$ eV) from a clean surface of metallic gold. It was checked by XPS that the irradiation of the sample with synchrotron radiation does not induce decomposition during the measurements.

3. Results and discussion

3.1. Near-edge x-ray absorption fine structure of $Si(CH_3)_nCl_{4-n}$ at the Si K and Cl K edges

Figure 1 shows the partial electron yields around the Si K edge as a function of photon energy for five kinds of $Si(CH_3)_nCl_{4-n}$ molecule condensed on Cu(110) (hereafter we call these curves NEXAFS spectra). The polar angle of the electric vector is 45° from the surface

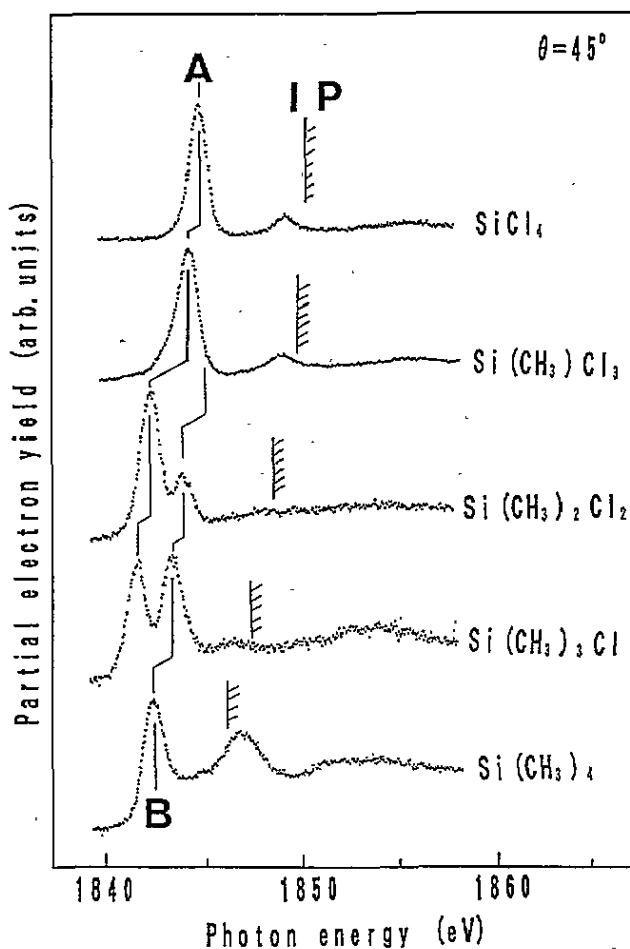**Figure 1.** Si K-edge NEXAFS spectra for a $Si(CH_3)_nCl_{4-n}$ $(0 \leqslant n \leqslant 4)$ multilayer adsorbed on Cu(110) at 90 K. The ionization potential (IP) indicated for each spectrum was determined from the kinetic energy of the Si 1s photoelectron in XPS.

normal. The number of layers was determined to be 600 by means of TPD measurements. The Si 1s ionization threshold indicated for each spectrum was determined by the kinetic energy of the Si 1s photoelectron in x-ray photoelectron spectra for the precisely calibrated photon energy excitation.

There have been several reports on the K-edge XANES spectra of $Si(CH_3)_4$ [8–14] and $SiCl_4$ [8–12, 15] in the gas phase. Also the XANES of gas-phase $Si(CH_3)_nCl_{4-n}$ $(0 \leqslant n \leqslant 4)$ molecules at the Si and Cl K edges has been systematically investigated by Ferrer *et al* [11]. The present spectral patterns at the Si K edge are essentially in good agreement with those obtained by Ferrer *et al* [11], but the resolution of the spectra is a little improved, and some new structures appear.

In all spectra, sharp resonance peaks (labelled A and B) are observed below the Si 1s ionization thresholds. If we adopt a one-electron transition (or single-particle) approximation, these peaks are ascribed to the resonances from Si 1s to the lowest unoccupied σ^* orbitals. For $SiCl_4$ or $Si(CH_3)_4$, only one resonance peak (peak A for

$SiCl_4$; peak B for $Si(CH_3)_4$ is observed. The lowest unoccupied molecular orbitals of these compounds are two antibonding states, i.e. a_1 symmetry containing a large amount of Si 3s orbital components and t_2 symmetry containing mainly Si 3p orbital components [16–18]. Considering the dipole selection rule, the allowed transition in the Si 1s excitation is the resonance excitation into the molecular orbitals with the t_2 symmetry. Thus peak A is virtually assigned to the excitation from Si 1s to the $\sigma^*(t_2)$ orbital of the Si–Cl bond and peak B to the $\sigma^*(t_2)$ orbital of the Si–C bond.

For compounds containing both chlorine and methyl groups $(Si(CH_3)_nCl_{4-n}, n = 1, 2, 3)$, two resonance peaks are seen below the ionization threshold. The relative intensity ratios of the two peaks in the mixed compounds are in good agreement with the ratio of the number of methyl groups to the number of chlorine groups. This implies that the lower-energy peaks (peaks A) are attributed to the excitation to the $\sigma^*(t_2)$ orbital around the Si–Cl bond, while the higher-energy peaks (peaks B) are assigned to that around the Si–C bond. Note that both peaks are shifted to higher energy with increase in the number of chlorine atoms. This is due to the increase in the Si 1s binding energy with the number of chlorine atoms, as was confirmed by the Si 1s x-ray photoelectron spectra.
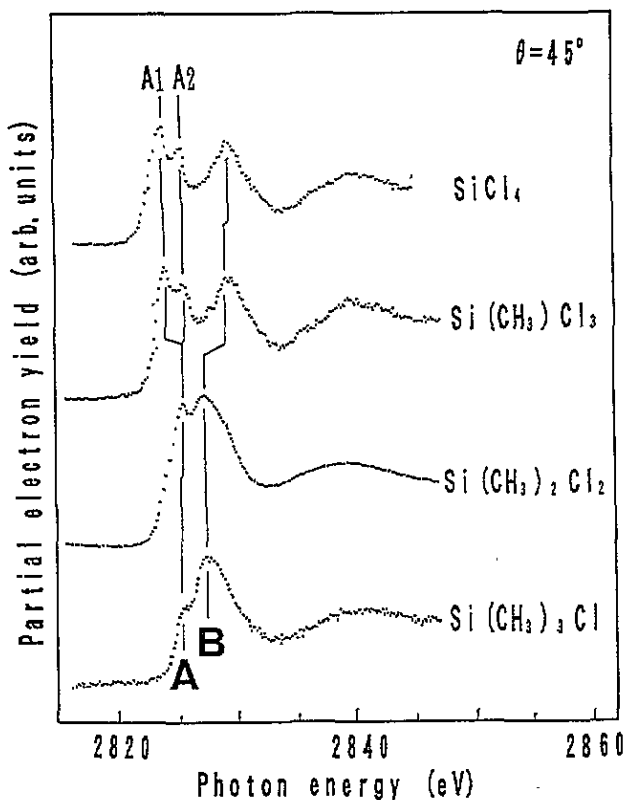

Figure 2. Cl K-edge NEXAFS spectra for a $Si(CH_3)_nCl_{4-n}$ $(0 \leqslant n \leqslant 3)$ multilayer adsorbed on Cu(110) at 90 K.

The NEXAFS spectra at the Cl K edge for the multilayer of four kinds of Cl-containing molecule are displayed in figure 2. At first glance, two resonances are observed in all

spectra. The lower-energy peak (A) is ascribed to the excitation from Cl 1s to the Si–Cl σ^* orbital. The higher-energy peak (B) is considered to be a double excitation, i.e. a shake-up satellite in which the valence electron is excited simultaneously with the Cl 1s→ σ^* excitation [11].

For SiCl₄ and Si(CH₃)Cl₃, peak A is further divided into two components (A₁ and A₂). It was reported that the lowest main unoccupied molecular orbitals in SiCl₄ are two antibonding orbitals, 8a₁ and 9t₂ [17]. The former mainly consists of Si 3s and Cl 3p components and the latter contains large amounts of Si 3p, and considerable amounts of Si 4d and Cl 3p components. Although the Si 1s electron is excited only into orbitals with t₂ symmetry, as was seen in figure 1, this is not the case in the Cl 1s excitation. Considering that the four chlorine atoms are electronically equivalent, both transitions into $\sigma^*(8a_1)$ and $\sigma^*(9t_2)$ become dipole allowed, unlike in the Si 1s excitation [11]. This leads to peak splitting (A₁ and A₂). It should be noted that the peak splitting is not due to the core orbitals with a₁ and t₂ symmetry because the four chlorine groups in this molecule are electronically equivalent and both 1a₁ and 1t₂ core orbitals have essentially the same binding energy. This was experimentally confirmed by the Cl 1s x-ray photoelectron spectra.

### 3.2. Polarization dependence of near-edge x-ray absorption fine structure for Si(CH₃)₃Cl and Si(CH₃)₂Cl₂

In the following, we shall deal with the molecular orientation of compounds containing both chlorine and methyl groups ($n = 1, 2, 3$) in the multilayered states. The polarization dependences of the NEXAFS spectra for multilayers of Si(CH₃)₃Cl and Si(CH₃)₂Cl₂ are shown in figures 3 and 4, respectively. The θ-value given for each spectrum represents the angle between the incident photon beam and the surface viewed from the top. The strong polarization dependence of the intensity ratio of the two resonance peaks is clearly seen for Si(CH₃)₃Cl (figure 3). Peak A almost disappears for the 7° incidence in which the electric vector is nearly perpendicular to the surface. At this incidence angle, the electrons from the Si 1s orbital cannot be excited into the σ^* orbitals which is parallel to the surface. This suggests that the Si–Cl axis of the multilayered Si(CH₃)₃Cl molecules is nearly parallel to the surface.

For Si(CH₃)₂Cl₂, on the other hand, the polarization dependence of the peak intensities is not clear (figure 4). This suggests that the Si(CH₃)₂Cl₂ molecules are randomly oriented in the condensed phase. We have also measured the polarization dependences of the NEXAFS spectra at the Si K edge for the other three compounds, but none of the NEXAFS spectra showed any polarization dependences.

The orientation of the molecular axis determined for the Si–Cl bond in Si(CH₃)₃Cl is supported by the polarization dependences of the NEXAFS spectra at the Cl K edge, which is presented in figure 5. Since these spectra are normalized by the total electron yield at 2820 eV where the polarization dependences do not exist, the intensity of the peak approximately represents the molecular orientation. The intensity of peak A originating from the Cl 1s→Si–Cl (σ^*) resonance decreases with decrease in the incidence angle, and this peak almost disappears at 7° incidence. This supports the above assumption that the Si–Cl bond is parallel to the surface.

3.3. Molecular orientation of adsorbed Si(CH₃)₃Cl

Now we shall determine the angles between Si–C (Si–Cl) bonds and the surface for Si(CH₃)₃Cl based on the polarization dependence of the Si 1s NEXAFS (figure 3). The adsorption angle hereafter is defined as the polar angle ω, which is the angle of the molecular
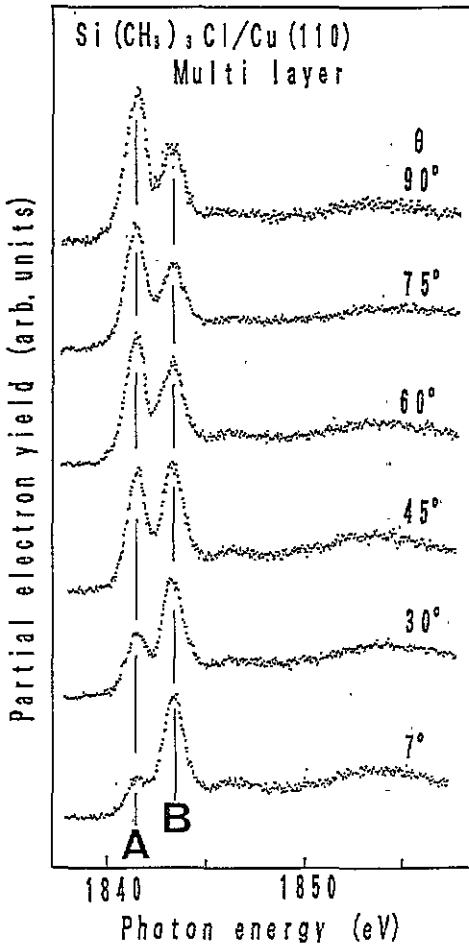
Figure 3. Polarization dependence of Si K-edge NEXAFS spectra for a Si(CH₃)₃Cl multilayer adsorbed on Cu(110) at 90 K. The θ-value for each spectrum represents the angle between the incident photon beam and the surface viewed from the top. Note that the angle between the electric vector and the surface corresponds to $(90 - \theta)°$.
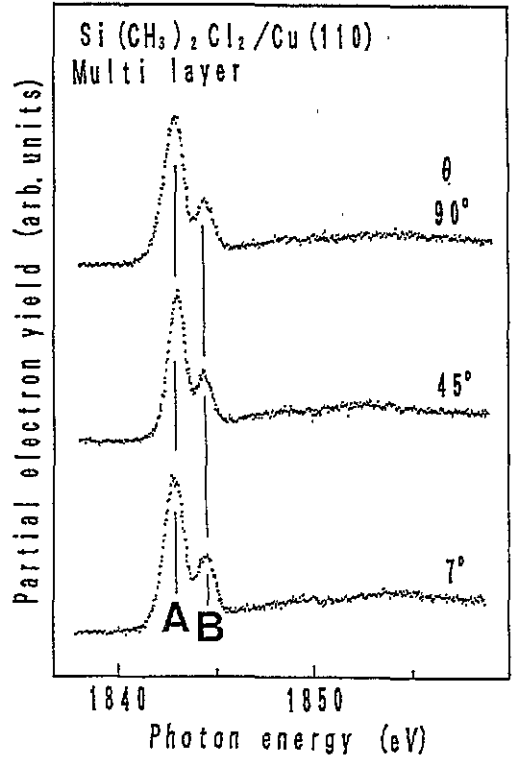
Figure 4. Polarization dependence of Si K-edge NEXAFS spectra for a Si(CH₃)₂Cl₂ multilayer adsorbed on Cu(110) at 90 K. The θ-value for each spectrum represents the angle between the incident photon beam and the surface viewed from the top.

axis measured from the surface normal. The resonance peak intensity $I(\theta)$ in the NEXAFS spectrum is given as [3, 19]

$$I(\theta) = A[PI_{p} + (1 - P)I_{v}] \tag{1}$$

where I_{p} and I_{v} are the transition intensities associated with the angle-dependent matrix elements parallel and vertical, respectively, to the electric vector, A is the normalization factor and P is the polarization factor. We have measured the dependence of $I(\theta)$ on the azimuthal angle, but no azimuthal-angle dependences were observed. This is probably because the condensed layer has a substrate symmetry higher than threefold. In this case, the intensities are expressed as [3]

$$I_{p} = \tfrac{1}{3}[1 + \tfrac{1}{2}(3\cos^{2}\theta - 1)(3\cos^{2}\omega - 1)] \tag{2}$$

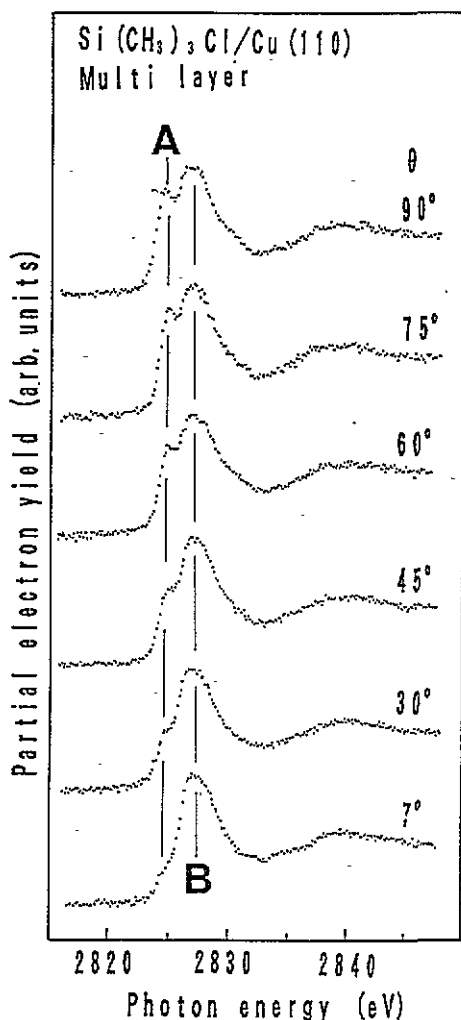**Figure 5.** Polarization dependence of Cl K-edge NEXAFS spectra for a Si(CH₃)₃Cl multilayer adsorbed on Cu(110) at 90 K. The θ-value for each spectrum represents the angle between the incident photon beam and the surface viewed from the top.

and

$$I_v = \tfrac{1}{2} \sin^2 \omega. \tag{3}$$

The polarization factor of the synchrotron beam in the present experimental condition is estimated to be about 0.95 [20]. The calculated values of $I(\theta)$ for various ω-values are plotted in figure 6 as a function of the value of $3\cos^2\theta - 1$. In this figure, the resonance intensities are normalized to be unity at the incident angle of $3\cos^2\theta = 1$. The normalized absorption intensities of the Si–Cl (σ^*) resonance fits in with the theoretical line for $\omega = 90°$. Considering the experimental errors, the polar angle of the Si–Cl bond is determined to be $\omega = 90 \pm 5°$. This confirms that the molecular axis of the Si–Cl bond is parallel to the surface.

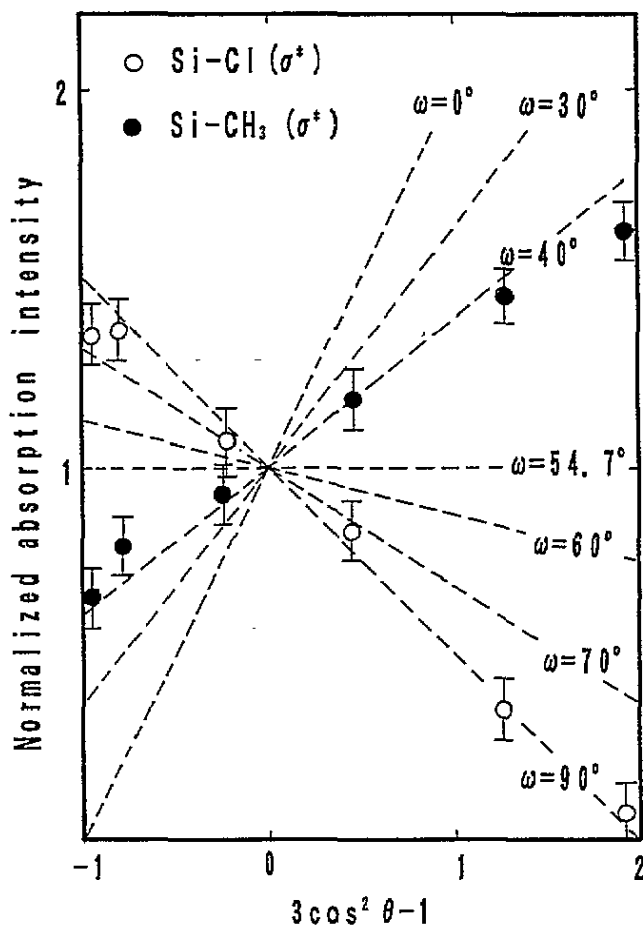**Figure 6.** Normalized absorption intensities of Si–Cl (σ^*) and Si–CH$_3$ (σ^*) resonances in the Si K-edge NEXAFS spectra for the Si(CH$_3$)$_3$Cl layer as a function of $3\cos^2\theta - 1$: – – –, theoretical lines when the σ^* bond is oriented to the polar angle shown as ω.

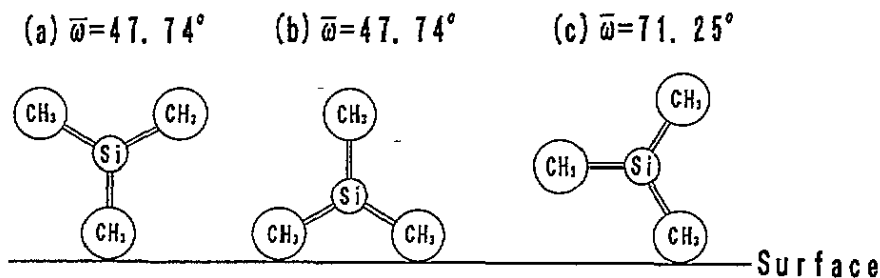(a) $\bar{\omega}=47.74°$ (b) $\bar{\omega}=47.74°$ (c) $\bar{\omega}=71.25°$

Figure 7. Three typical configurations of Si–C bonds viewed from the molecular C$_3$ axis. The averaged value of the polar angles of the three Si–C bonds is indicated as $\bar{\omega}$ in each figure.

On the other hand, the normalized absorption intensities of the Si–CH$_3$ (σ^*) resonance approximately fits the line for $\omega = 43°$. Considering the experimental errors, the polar

angle of the Si–C bond is determined to be $43 \pm 5°$. This value represents the averaged value of the polar angles of the three Si–C bonds. If we assume that the Si–C bonds are rotated around the molecular C_3 axis (Si–Cl bond), the average polar angle is calculated to be $50°$. The present result is slightly lower than the averaged value. Figure 7 shows the typical three configurations of the Si–C bonds, which are viewed from the Si–Cl axis when we assume that the Si–Cl bond is parallel to the surface. The average polar angle $\bar{\omega}$ is shown in each configuration. Although we cannot determine which configuration is dominant as to the Si–C bond, the configuration in figure 7(c) can be apparently excluded, and the former two configurations (figures 7(a) and 7(b)) are plausible.

In the present work, we have measured the polarization dependence of thinner films up to 12 layers, and also we have examined the condensed layers on the other substrate such as Ni(111) and Pt(111). However, neither the thickness nor the substrate has any effect on the specific orientation of the $Si(CH_3)_3Cl$ molecule. Therefore we consider that the origin of the specific orientation for this molecule is related to the intrinsic property of this molecule itself, such as the large dipole moment of $Si(CH_3)_3Cl$ compared with the other molecules. Further experiments for the NEXAFS of the monolayer or submonolayer and temperature effect on the molecular orientations are now in progress to elucidate this point.

4. Summary

We have measured the molecular orientations of the condensed layers of $Si(CH_3)_nCl_{4-n}$ $(0 \leqslant n \leqslant 4)$ molecules by means of NEXAFS measurements. Although these molecules consist of only a σ bond, the NEXAFS at the Si K edge splits into two peaks when the Si atom is coordinated to both CH_3 and Cl groups $(n = 1, 2, 3)$. The two peaks were assigned to the resonances from Si 1s to Si–Cl (σ^*) and Si–CH_3 (σ^*) orbitals, respectively. A clear polarization dependence was observed in the NEXAFS spectra at the Si K edge only for $Si(CH_3)_3Cl$. On the basis of the incidence angle dependences of the peak intensities of the two resonances, it was concluded that the Si–Cl bond is parallel to the surface and the average polar angle of the Si–CH_3 bonds is about $43 \pm 5°$.

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