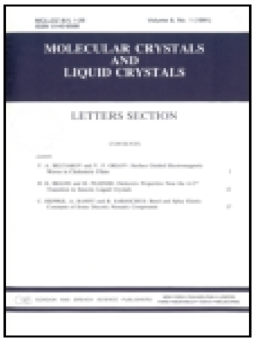

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Investigation of Unoccupied Electronic States near the Fermi Level of Polysilane using Resonant Auger Spectroscopy

HIROSHI OGAWA,[1,*] HIROMI IKEURA-SEKIGUCHI,[1]
AND TETSUHIRO SEKIGUCHI[2]

[1]Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan
[2]Quantum Beam Science Center, Japan Atomic Energy Agency (JAEA), Tokai-mura, Japan

*Unoccupied electronic states near the Fermi level of poly(dimethylsilane) were probed using Si 1*s *X-ray absorption spectroscopy (XAS) and Si* $KL_{2,3}L_{2,3}$ *resonant Auger spectroscopy (RAS). The measured resonance peaks of XAS spectra near Si* K*-edge have been assigned in comparison with the discrete variational (DV)-Xα molecular orbital calculations. The rapid delocalization of Si 1*s *core-excited electron through the empty conduction band was observed along the polymer chain with the energy-dependent RAS measurement, and the electron delocalization time was estimated based on the core-hole clock method.*

Keywords X-ray absorption spectroscopy; resonant Auger spectroscopy; polysilane; σ-conjugated polymer; core hole clock

Introduction

Polysilanes are σ-conjugated organic polymers with a one dimensional silicon-silicon backbone. They have unique electronic and optical properties, such as photoconductivity with a high hole mobility [1, 2], large nonlinear optical effects [3, 4], and a high quantum efficiency photoluminescence [5] due to the delocalized σ-electron along the Si main chain. In this paper, unoccupied electronic states of poly(dimethylsilane) (PDMS) have been studied by X-ray absorption spectroscopy (XAS) near the Si *K*-edge [6] and Si $KL_{2,3}L_{2,3}$ resonant Auger spectroscopy (RAS). To investigate the electron-transport property of an unoccupied conduction band state of Si chains, the excitation energy-dependent RAS measurement was performed. The energy-dependent RAS provides information on the core-excited electron delocalization rates with chemical specificity. In a polymer system, there are two competing Auger decay channels, known as spectator and normal Auger decay, which correspond to core-excited electron localized and delocalized in the vicinity

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[*] Address correspondence to H. Ogawa, Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan. E-mail: ogawa.h@aist.go.jp

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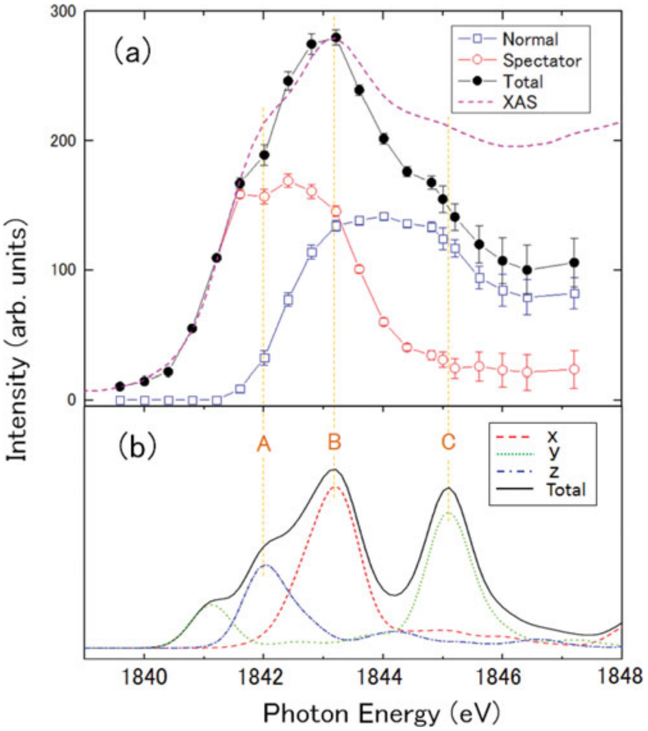

Figure 1. (a) Si *K*-edge XAS spectrum for poly(dimethylsilane) (PDMS) (broken line) and the integrated intensities of resonant Auger spectra as a function of excited photon energy. Integrated intensities of normal (open square) and spectator (open circle) Auger components and the sum of these two components (closed circle) are plotted. (b) Oscillator strength spectra of PDMS calculated by the DV-Xα molecular orbital method. The Si backbone lies in the x direction (broken line) and the methyl side chains in the yz plane (dotted and dotted broken lines for y and z directions, respectively).

of a core-hole site during the core-hole life time, respectively (see figure 1 of ref.[10]). The two Auger channels can be distinguished in the energy-dependent RAS, since the kinetic energy of outgoing Auger electron has different dispersive behavior between these two processes. For quantifying the delocalization property of the band, we also examined the delocalization time of resonantly excited electron in terms of core-hole clock method [7–10], which is based on usage of a core-hole life time as an internal reference clock. Because the relative intensity of the different decay channels is proportional to the relative decay rates, the electron delocalization time can be determined from the measured ratio of spectator to normal intensities in RAS and the core-hole life time. This method has been applied to research on ultra-fast charge transfer dynamics in the time scale of a few femtoseconds [8] down to a few hundred attoseconds [9] that the conventional method such as laser pump-probe technique is difficult to address.

Experimental

PDMS powder (Gelest, Inc) with an average molecular weight of 2000 was used for XAS and RAS measurements. The as-received powder sample of PDMS was mounted on a

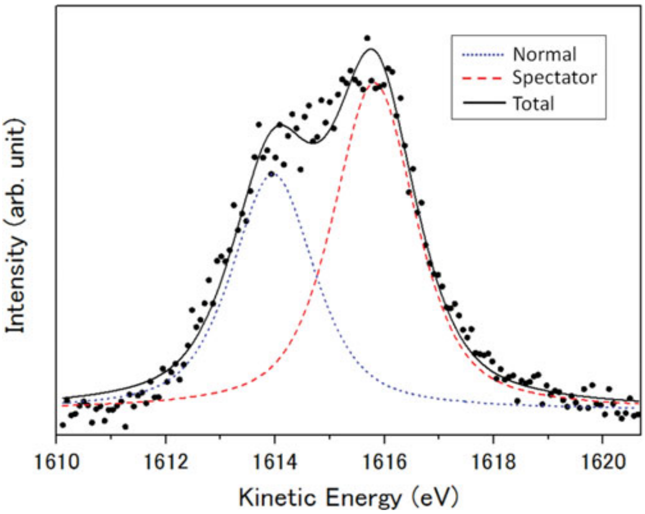

Figure 2. Si *KLL* resonant Auger spectrum for PDMS measured at excited photon energy of 1842.8 eV. The dots and the solid lines are shown as the experimental data and a least-square fit, respectively. Normal (dotted line) and spectator (broken line) Auger features are visible with total Auger yields (solid line).

conducive carbon tape. These experiments were carried out at room temperature on the beamline BL-27A [11] of the Photon Factory, High Energy Accelerator Research Organization (KEK-PF), Tsukuba, Japan. The synchrotron radiation from the bending magnet was monochromized by an InSb(111) double-crystal monochromator with an energy resolution of ca. 0.8 eV around Si *K*-edge. The XAS spectra were measured by taking sample drain current near the Si *K*-edge. The photon energy was calibrated by referencing to the resonance peaks of XAS spectra for PDMS of Mannan et al [12]. The RAS measurements were performed using a hemispherical electron-energy analyzer [CLASS-100; Vacuum Science Workshop (VSW)], operating in a constant pass energy mode of 44 eV.

Results and Discussion

The measured XAS spectrum of PDMSnear Si *K*-edge is shown in Fig. 1 (a). Three resonance peaks (marked as A, B and C) were observed in the energy range of 1840 – 1848 eV. To assign the XAS peaks, the oscillator strength of a model cluster for PDMS, i.e. $CH_3[Si(CH_3)_2]_8CH_3$, was theoretically calculated. Since the most stable conformation of PDMS is planar zig-zag [13], the structure with an all-trans Si backbone was optimized by the B3LYP functional with a 6-31G* basis-set [14]. Core-hole excited states for the optimized geometry were calculated using the discrete variational (DV)-Xα molecular orbital method [15]. Relaxation due to the existence of a core hole is considered using Slater's transition state theory, i.e., half of the electrons in a core orbital are removed and half of them occupy unoccupied molecular orbitals. Here, a hole is created in the 1*s* orbital for the fourth (center) silicon atom from the left in the cluster. In Fig. 1(b), the theoretical spectra convoluted with a Gaussian function of a width of 0.8 eV (FWHM) are plotted with an energy shift of –0.6 eV. Compared with the calculated spectra, peak B can be assigned to the resonance excitation from Si 1*s* to σ^*(Si–Si) unoccupied states, whereas the peaks A

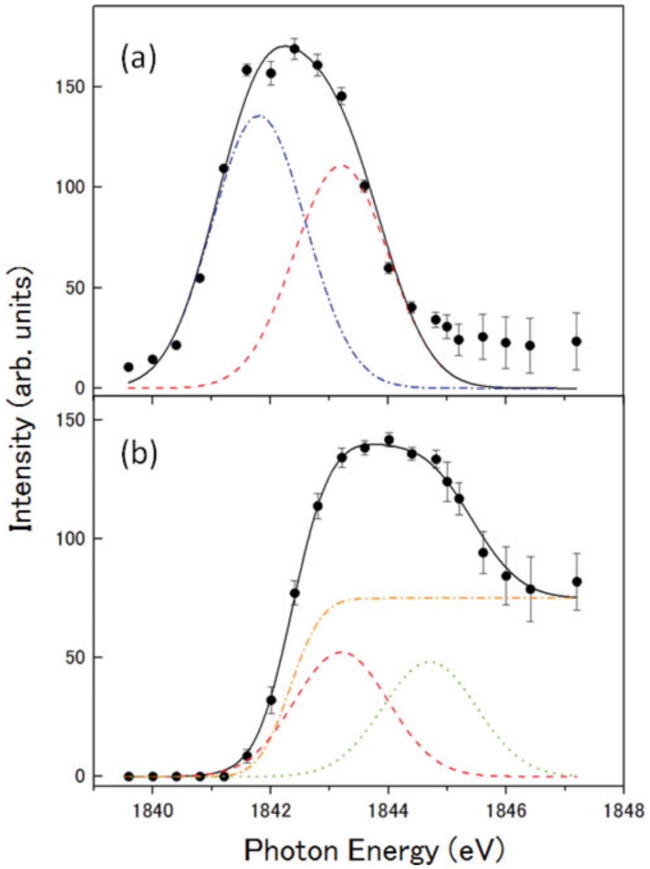

Figure 3. Integrated intensities of (a) spectator and (b) normal Auger components. The experimental data and results of the least-square fit are described as closed circles and black solid lines. The fitting results were decomposed into two Gaussian function (blue dotted broken, red broken and green dotted lines corresponding to the peaks A, B and C, respectively, in Fig. 1) and an error function (orange dotted broken line) for the continuum state.

and C to σ^*(Si–C). Our assignment is consistent with the previous studies of polarization dependent XAS for PDMS [12] and poly(di-n-hexylsilane) [16].

To make a detailed study on electron delocalization property of the unoccupied conduction band, we carried out the measurement of the excitation energy dependence of Si $KL_{2,3}L_{2,3}$ RAS. A typical RAS spectrum for PDMS is shown in Fig. 2, which was analyzed by curve fitting with two Voigt function. The peak at higher kinetic energy is assigned to spectator Auger feature, while the peak at lower energy as normal Auger because the shift of spectator Auger to higher kinetic energy is caused by the screening of a core-hole by the localized spectator electron, which is so-called as spectator shift [7].

Partial yields for normal and spectator Auger final states were obtained by measuring the each peak area as a function of photon energy. In Fig. 1(a), the integrated intensities of normal and spectator Auger components are plotted. The spectra shape of the sum of these two components shows reasonable agreement with that of XAS. Considering the energy positions for the three features in Fig. 1(a), the spectator Auger component is significantly contributed from the features A and B, and the normal Auger component from the contributions B and C.

Figure 3 shows the results of curve fitting for normal and spectator Auger components. The spectator Auger spectrum was fitted by two Gaussian function corresponding to localized components of the peaks A and B. As for the normal Auger component, the spectrum was deconvoluted into two Gaussian peaks corresponding to delocalized components of the peaks B and C and an error function for continuum step. Such delocalized feature below the energy of continuum state was observed at the peak B, which indicates that σ^*(Si–Si) orbitals are extended along the Si chains.

We have applied the core-hole clock method to investigate the electron delocalization time τ_{ED} of the Si 1s core excited state through the empty conduction band. The delocalization time τ_{ED} can be determined from the ratio of the intensity of spectator (I_{2h1e}) to normal (I_{2h}) components, as $\tau_{\mathrm{ED}} = \tau\ (I_{\mathrm{2h1e}}/\ I_{\mathrm{2h}})$ [7, 10]. The core life time τ was taken to be 1.4 femtoseconds, which was derived from a lifetime width of 0.48 eV for Si 1*s* [17]. As a result, the delocalization time τ_{ED} was deduced to be ca. 1.5 femtoseconds at the delocalized peak maximum (peak B) of 1843.2 eV.

Summary

We have investigated unoccupied electronic states near the Fermi level of PDMS using Si 1*s* XAS and Si $KL_{2,3}L_{2,3}$ RAS. The three resonance peaks of XAS spectrum for Si 1s in the near edge region were assigned based on the DV-Xα calculations. The resonance peak of XAS spectrum at excitation energy of 1843.2 eV was assigned to be the resonance excitation from Si 1*s* to σ^*(Si–Si) unoccupied states, and the other two peaks were that from Si 1*s* to σ^*(Si–C). The electron delocalization of the core-excited electron through the conduction band state was observed along the Si chains using the energy-dependent RAS near the Si *K*-edge. We deduced the electron delocalization time τ_{ED} as ca. 1.5 femtoseconds using the core-hole clock method.

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