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Self-ordering of polysilanes on metal and semiconductor surfaces investigated by X-ray absorption spectroscopy

Md. Abdul MANNAN[1,2], Yuji BABA*[1], Tetsuhiro SEKIGUCHI[1], Iwao SHIMOYAMA[1], Norie HIRAO[1], Masamitsu NAGANO[2], Hideyuki NOGUCHI[2]
[1]Japan Atomic Energy Agency, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan
[2]Department of Chemistry and Applied Chemistry, Saga University, Saga 840-8502, Japan

Introduction

Polysilanes composed of silicon-silicon backbone have excellent properties in comparison with carbon-based polymers. One of the outstanding features is high electric conductivity along the one-dimensional chain due to smaller HOMO-LUMO band gap. The polysilane is considered as an ideal one-dimensional molecular wire with high electric conductivity. Also, thin films of polysilanes have outstanding physical properties such as photoconductivity and ultraviolet electroluminescen-ce [1]. The electric and optical properties in thin films of one-dimensional polymers strongly depend on the molecular orientation. Therefore, it is very important to precisely determine the orientation of polymers on substrates. In this study, the molecular orientations of polydimethylsilane (PDMS) on metal and semiconductor surfaces have been studied.

Experimental

All the experiments were performed *in situ* at the end station of BL-27A. Indium tin oxide (ITO) and highy oriented pyrolytic graphite (HOPG) have been used as the substrates. The evaporation was performed by electron-bombardment heating. The evaporation rate was presicely controlled by monitoring the positive current of the shutter. The electronic structure and molecular orientation were precisely investigated by XPS and NEXAFS measurements. The NEXAFS spectra were taken with the total electron yield mode by recording the sample current.

Results and discussion

Fig. 1 shows the Si *K*-edge NEXAFS spectra taken at different incident angles. The spectral features are almost the same as those previously reported [2]. The NEXAFS spectra for the films on ITO and HOPG have at least four resonance peaks of which two peaks are found to be strongly polarization dependent. The low-energy peak A at 1842.0 eV has short-axis polarization due to the resonance excitation from Si 1s σ* p_{yz} orbital corresponding to the Si–C bond. Whereas, the high energy resonance peak B at 1843.2 eV has long-axis polarization due to the resonance excitation from Si 1s σ* p_x orbital corresponding to the Si–Si bond [3]. Intensity of the peak A decreased and intensity of the peak B increased when incident angle becomes low. Quite opposite phenomenon has been observed for the peaks on HOPG. On the basis of polarization dependency, the PDMS molecules are self-ordered and the backbones of the films are perpendicularly oriented to the ITO. From the quantitative analyses of the peak intensities as a function of the incident angle of X-rays, it is supposed that the PDMS have standing-up orientation with helical conformation rather than zig-zag structure [4]. It was found that the molecular orientation of the PDMS on HOPG surface is reverse to those on ITO surface. The polarization dependences revealed that the backbones of the PDMS molecule are nearly parallel to the HOPG surface.

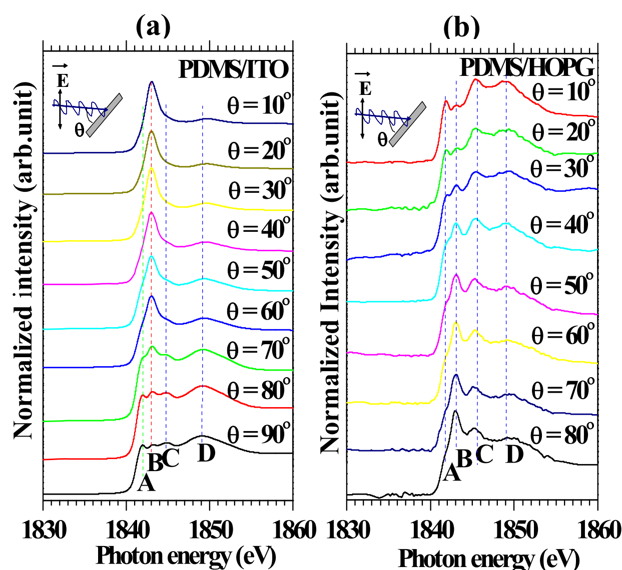

Fig. 1. Si *K*-edge NEXAFS spectra taken at different incident angles of the SR beam for the samples on (a) ITO and (b) HOPG, respectively.

References

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* baba.yuji@jaea.go.jp