

Orientation of one-dimensional silicon polymer films studied by polarization-dependent NEXAFS

Md. Abdul MANNAN^{1,2}, Yuji BABA^{*1}, Tetsuhiro SEKIGUCHI¹, Iwao SHIMOYAMA¹,
Norie HIRAO¹, Masamitsu NAGANO², Hideyuki NOGUCHI²

¹Japan Atomic Energy Agency, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan

²Department of Chemistry and Applied Chemistry, Saga University, Saga 840-8502, Japan

Introduction

Polysilanes composed of silicon-silicon backbone are considered to be ideal one-dimensional (1D) molecular wires with high electric conductivity. It has also been predicted that the polysilanes possess electronic structure similar to direct band-gap semiconductor. Since the electric and optical properties in thin films of 1D polymer strongly depend on the configuration of the molecular skeleton, it is much important to determine the precise molecular orientation of polymers on solid surfaces. In the previous paper, we have reported that the Si-Si skeleton of polydimethylsilane (PDMS) deposited on indium tin oxide (ITO) surface is perpendicularly oriented, and the polymer has a helical conformation rather than zig-zag structure with polar angle around 40° [1]. In this report, we present the results for the orientation of PDMS films grown on highly oriented pyrolytic graphite (HOPG) substrate and the results are compared with the previously obtained ones.

Experimental

All the experiments were performed *in situ* at the BL-27A station. The PDMS powder was evaporated by electron-bombardment heating. The evaporation rate was precisely controlled by monitoring the positive current of the shutter. The molecular orientations were investigated by Si *K*-edge NEXAFS measurements. The NEXAFS spectra were taken with the total electron yield mode.

Results and discussion

Fig.1(a) shows the Si *K*-edge NEXAFS spectra taken at different incident angles for 1.25 nm layer. The spectra show at least four resonance peaks of which two peaks are found to be strongly polarization dependent. The peak A is due to the resonance excitation from Si 1s to σ^* p_{yz} orbitals (plane type) localized at the Si-C bond, and the peak B corresponds to the resonance from Si 1s to σ^* p_x orbitals (vector type) localized at the Si-Si bond [2]. Fig.1(b) displays the normalized intensities of the peaks A and B as functions of the incident angle θ [3]. The filled circles are the experimental values. It is observed that the experimental values of the polar angles for both the vector and plane type orbitals follow the theoretical lines around 65°.

If the structure is flat-lying helical, $\alpha=48.5^\circ$, and $\gamma=41.5^\circ$. For the flat-lying zig-zag configuration, there are two cases. One is that the Si-C plane is perpendicular to

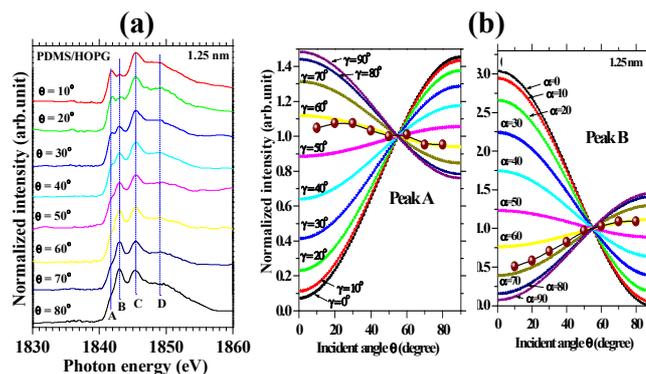


Fig.1 (a) Si *K*-edge NEXAFS spectra taken at different incident angles for multilayered PDMS film on HOPG. (b) Normalized intensity I of the peaks A and B in the NEXAFS spectra as a function of the incident angle θ . The filled circles are the experimental values.

the surface. In this configuration, $\alpha=54.5^\circ$ and $\gamma=0^\circ$. The second case is that the Si-Si bond is parallel to the surface. In this configuration, $\alpha=90^\circ$ and $\gamma=0^\circ$. The experimental data show that $\alpha=65^\circ$, and $\gamma=65^\circ$. The values are not exactly the same as those of the flat-lying helical structure. But if the configuration is flat-lying zig-zag, at least γ -value should be nearly 0 for both cases. Thus we tentatively assign that the configuration is flat-lying helical with the polar angle of around 65°.

As to the question why the orientations of the PDMS molecules are opposite between HOPG and ITO surfaces, we consider as follows. PDMS molecules lie down along the surface morphology through van-der-Waals force. The ITO surface is vertically undulated in the order of 10 nm. Therefore, the first layer of PDMS on ITO cannot lie down due to the stress, so PDMS molecules stand-up. On the other hand, HOPG has perfectly flat surface without defects and steps, so the first layer of PDMS can lie flat along the surface. It is considered that the succeeding over layers follow the orientation of the first layer.

References

- [1] M.A. Mannan *et al.*, J. Electron Spectrosc. Relat. Phenom. **181**, 242 (2010).
- [2] V.R. McCrary *et al.*, J. Chem. Phys. **88**, 5925 (1988).
- [3] J. Stöhr, XEXAFS spectroscopy, Springer (1996).

* baba.yuji@jaea.go.jp