

Polarized NEXAFS observation of the in-plane anisotropy in a highly oriented poly(3-alkylthiophene) thin film

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Introduction

Poly(3-alkylthiophene) (PAT) is a solution-processable conjugated polymer, and attracting much attention as an organic semiconductor material for optical and electronic devices [1]. It is known that characteristics of the PAT thin film are strongly affected by the changes in the π - π interaction between polymer main chains, and in the dimensionality of the film [2]. Thus, it is important to fabricate an in-plane ordered PAT thin film for elucidating the relationship between the film structure and the physical properties. In this study, we tried to control the in-plane ordering of the PAT thin film by growing on a specially designed substrate, on which straight step/terrace structures are periodically arranged. The structure of the PAT film grown on this surface was characterized by polarized near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

Experimental Section

A 4°-off vicinal Si(111) surface was thermally cleaned under ultrahigh vacuum condition by the direct current heating, and the step-bunching was caused by annealing and cooling the surface under adequate conditions [3]. After these processes, periodically arranged straight step/terrace structures were fabricated on the Si surface, as shown in Fig. 1. Next the substrate surface was made hydrophobic by fabricating a self-assembled monolayer of octadecyltriethoxysilane. After this treatment, 5 layers of poly(3-dodecylthiophene) (PDT) were deposited from the PDT monolayer spread onto Milli-Q water by the horizontal lifting technique.

Results and Discussion

Fig. 2 shows polarized S *K*-edge NEXAFS spectra, measured at three azimuthal angles, of the PDT film on the hydrophobic step-bunched Si surface. Here, the incident angle of the *p*-polarized X-ray from the surface normal was 0°. These spectra clearly exhibited in-plane anisotropy, namely that the intensity of the S 1s- σ^* (S-C) transition peak was the strongest when the *E*-vector plane of incident *p*-polarized X-ray was parallel to the straight steps on the substrate surface. Since the σ^* transition moment is parallel to the polymer main chain axis, it is suggested that the transferred PDT molecules are more preferentially elongated along the one-dimensional

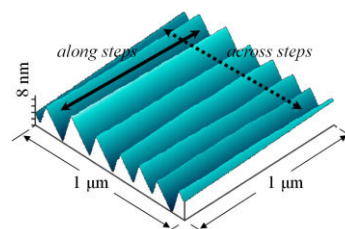


Fig. 1 An AFM image of a step-bunched 4°-off Si(111) surface.

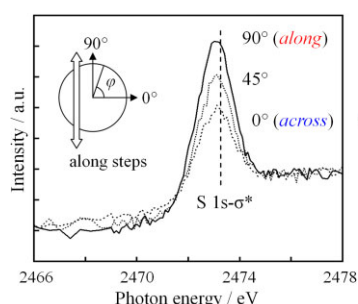


Fig. 2 Azimuthal angle dependence of the NEXAFS spectra of a PDT film on a step-bunched surface.

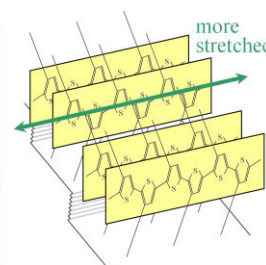


Fig. 3 A schematic illustration of the anisotropic orientation of the polythiophene molecules on the step-bunched surface.

periodic structures than the direction across these structures, as shown in Fig. 3. Contrary, no distinct azimuthal angle dependence was recognized in NEXAFS spectra of a PDT film deposited on a flat hydrophobic Si surface. In addition, AFM observation revealed that the PDT film on the step-bunched surface was smoother than that on the flat surface. We conclude from these results that the step-bunched substrate is effective in controlling the in-plane molecular orientation in the PAT thin film.

References

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